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MONOGRAPH No. III
NATIONAL RESEARCH COUNCIL
COMMITTEE ON ELECTRICAL INSULATION
J. B. WHITEHEAD, CHAIRMAN
THE JOHNS HOPKINS UNIVERSITY, BALTIMORE, MD.

**THE ELECTRICAL
PROPERTIES OF GLASS**

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the Committee on Electrical Insulation
Division of Engineering and Industrial Research
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GLASS**

By J. T. LITTLETON, Chief, Physical Labora-
tory, Corning Glass Works; and G. W. MOREY,
Member of the Staff, Geophysical Laboratory,
Carnegie Institution of Washington. 184 pages.
6 by 9. 69 figs. Cloth.

THE ELECTRICAL PROPERTIES OF GLASS

BY

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FOREWORD

THIS, the third in the series of monographs issued under the auspices of the Committee on Electrical Insulation, N. R. C., appropriately deals with a solid, the two preceding having treated gases and liquids, respectively. The solids are the most numerous and most important insulating materials. The word solid is to be understood as including not only those solids of simple chemical structure, but the whole range of complex materials having insulating properties adapted to particular purposes which maintain their form and condition throughout a normal temperature range. All such materials are highly anomalous from the standpoint of classical dielectric behavior, and in most cases the variation of the more important electrical properties must be studied and analyzed separately.

Among this class of materials glass is an outstanding example. It offers itself with manifest advantages for a number of particular classes of insulation, and in some of its forms may attain exceptional values of dielectric strength, resistivity, and dielectric loss. Heretofore, no sufficient theory and little orderly knowledge have been available as to the relation between electrical properties of glass and its composition, method of assembly, and other features bearing on its ultimate behavior as an insulator. The present volume, therefore, with its wide survey of the literature, and the authoritative viewpoints of its experienced authors, should fill an important need of all students of dielectrics as insulators.

J. B. WHITEHEAD, *Chairman.*

THE JOHNS HOPKINS UNIVERSITY

June 21, 1933

PREFACE

GLASS is one of the oldest materials used for electrical insulation. In recent years new glasses have been developed which have properties essentially different from the older glasses and hence have a wider field of application to insulating problems. In addition glass has been repeatedly used for a study of the fundamental electrical properties of solid insulating materials. So far no attempt has been made to collect and critically review the available information bearing on glasses. Consequently the Sub-Committee on Physics of the Committee on Electrical Insulation of the National Research Council requested that a summary be made of our present state of knowledge as to the electrical properties of glasses.

This work is primarily intended as a reference for laboratory workers interested in electrical measurements and dielectric theory. However, glass is an engineering material so some attention has been given to its use and to its limitations as this is of practical interest to insulation engineers.

In order that the reader might have a better understanding of the general subject of glass and of the different types of existing glasses, the first chapter is devoted to a general discussion of the manufacture of glassware and to the physical and chemical properties of the different glasses. The second chapter deals with the surface and volume conductivity studies and the last three chapters more particularly with the dielectric properties of glasses. An attempt is made throughout to emphasize the deficiency of the existing data and the limitations of our present knowledge in the hopes that further research will be forthcoming.

J. T. LITTLETON.
G. W. MOREY.

June 1, 1933.

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THE ELECTRICAL PROPERTIES OF GLASS

CHAPTER I

THE MANUFACTURE, COMPOSITION AND PROPERTIES OF GLASS

1. Definition of Glass.—For the purpose of this monograph, glass will be defined as an industrial material obtained by melting together various inorganic oxides, or compounds that yield oxides by decomposition during the melting process, and so cooling the resulting solution that crystallization does not take place. The product usually, but not always, is transparent, is permanent in the air, and possesses high elasticity, great strength, and high electrical resistivity. Each one of these characteristic properties may be altered within limits by changing the nature and proportions of the ingredients melted. The properties of glass are determined primarily by the composition.

2. The Manufacture of Glass.—Glass is made either by an intermittent melting process, in which individual containers, or pots, are heated in suitable furnaces, or by a continuous process in a tank. Intermittent methods have been used since the beginning of glass manufacture, and are so especially suited for many types of operation that they probably never will be entirely displaced, though there is obvious commercial advantage in the continuous tank process.

For purposes of experimental study, glasses have usually been melted in platinum crucibles, heated either in gas or in electric furnaces; such a procedure is particularly adapted to a well-controlled study of the properties of glass as a function of the composition.

Optical glass is melted in fire-clay "pots" of one to three thousand pounds' capacity, in which it is allowed to cool, and the pot can be used only once. In most large-scale manufacturing of other than optical glass, however, the glass is poured, ladled, or gathered from the pot while still fluid, and the pot is used repeatedly.

Glass pots are made from refractory clays, and the better and more resistant ones approach porcelain in composition.

An increasing proportion of modern glassware is made in tank furnaces, which are characterized by the furnace's being itself the container for the fluid glass. Such furnaces are gas or oil fired either by the regenerative or recuperative process, with the gas ports arranged along the sides or at one end so as to direct the flames out over the glass pool. The whole is covered with a low refractory roof either domed or arched. In the operation of the tank furnace the raw materials (sand, lime, soda, potash, etc., commonly called "batch") are fed in at one end, and the glass is withdrawn at the other. There is usually a single partition or "bridge wall" separating the tank into a "melting end" and a "working end" which are connected below the glass surface. Those parts of a tank that are in contact with the glass are constructed of refractory pieces known as tank blocks. They must be as resistant as possible to solution in the glass. This problem of corrosion resistance has probably been solved more successfully for tank blocks than for the pots used in the intermittent melting process.

Tank furnaces are adapted for continuous operation and large-tonnage automatic manufacture, for which reasons they are used almost exclusively in serving the numerous types of continuous glass-forming machines. The glass produced from tank furnaces is more uniform in composition than glass melted in pots, unless the pots are stirred, as in the manufacture of optical glass.

After the glass is thoroughly melted and freed from

bubbles, that is, "fined" or "planed," it is "worked," in which stage it is subjected to a shaping operation while cooling. Plate glass is sometimes formed by pouring from the melting pot onto a large table, then rolling into sheets. Sometimes it is drawn in a continuous sheet directly from the tank. Window glass formerly was blown into cylinders by hand operatives, who were later replaced by a machine which drew much larger cylinders than were possible by hand labor. In either case the cooled cylinder had to be split and the two halves separately flattened by reheating. At present most window glass is drawn directly from the surface of the tank in sheets, although the cylinder process is still used to some extent. Heavy ware, such as signal lenses, cooking ware, flat plates, or electrical insulators, are pressed in cast-iron or alloy-steel molds, the glass being fed in either by hand or by automatic feeders. Hollow ware is formed by a blowing process, sometimes by hand labor without the use of molds, sometimes by hand labor and molds inside of which the glass is blown to its final shape; but by far the greater part of blown ware is made on automatic machines, fed with glass from a tank. In the manufacture of bottles, fruit jars, and such ware, the automatic machine commonly used shapes the blank to be blown by a pressing operation; hence the machines are known as "press and blow" machines.

By way of illustration of automatic machine production, one of the most modern and refined processes will be briefly described. Electric-light bulbs are made in enormous quantities by continuous machine production, of which the most interesting example is the Corning machine, which has a capacity as high as 622,000 bulbs per 24-hour day and is completely automatic. The method of operation of this machine will illustrate automatic glass blowing and can be explained with the aid of Fig. 1. The glass flows in a continuous stream from the forehearth of a tank and passes between two rollers which deliver a

continuous narrow ribbon of glass. One roller has depressions on its surface, giving a series of uniformly spaced thick buttons along the ribbon, which fit over the successive openings in an endless metal belt. The ribbon of molten glass is carried by the belt in a straight line under a row of blow-heads, forming a second endless chain moving in time with, and above, the first. As the belt moves on, the glass buttons sag through the belt openings, and the blow-heads register above them, after which each lengthening bulb of glass is enclosed from below by a split

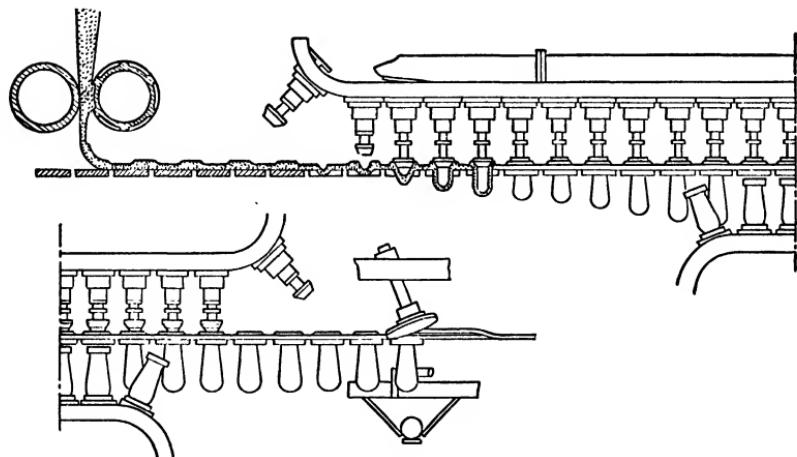


FIG. 1.—The Corning 399 Bulb Machine.

rotating metal mold, and the finished bulb is blown as it moves forward in its place in the line by air admitted from the wind-box. After the bulb has cooled enough to maintain its shape, the molds open, as shown in the lower part of Fig. 1, and the bulb is separated from the glass ribbon and directed into an annealing chamber, where objectionable strains are removed.

The Annealing of Glass.—All kinds of glassware are usually subjected to an annealing process for the purpose of regulating the internal stresses. The mechanism of the introduction of strain into glass and the proper procedure for its removal by annealing are now clearly understood,

and it is probable that glass can be obtained with less internal stress than any other material. The best possible annealing is required for glass used for optical purposes, but for most uses a moderate amount of strain, suitably distributed, is desirable because it makes the glass less liable to breakage.

Strain in glass is detected by means of its effect on polarized light, which is similar to that of a birefracting crystal. This was discovered in 1813 by Brewster, who found that a glass plate under load behaves as a uniaxial negative crystal, the optic axis being the direction of application of the load; and that the birefringence, as measured by the path difference of the two plane polarized light waves formed on traversing the strained block is proportional to the strain. The birefringence thus serves as a direct measure of the amount of strain, but the relation between stress and strain depends on the composition of the glass.

It will be instructive to consider the source of strain in glass and the manner of its production.¹ Suppose that a flat plate or slab of glass, which is assumed to be long enough so that end effects may be neglected, originally free from stress, and at a uniform and comparatively low temperature, is heated at both faces, that is, at the two surfaces normal to the shortest dimensions of the piece. The outside layers become hotter and tend to expand more than the inner layers; that is, the surfaces of the slab are not free to expand the normal amount and will therefore be under longitudinal compression in all directions parallel to the surface of the slab. At the same time the innermost layers will be stretched by the outer layers and will be under tension. The longitudinal stress changes continuously from a compression at the surface to a tension in the middle, and therefore at a certain distance below each

¹ The discussion of this subject follows closely that of L. H. Adams and E. D. Williamson, *J. Franklin Inst.*, 190, 597 (1920), and much of it is direct quotation.

surface there will be a layer with no stress, i.e., a neutral zone. If now the temperature in the slab be allowed to become uniform throughout, thus regaining its original condition, the thermal gradient and the resulting stresses will disappear. On the other hand, if the glass be cooled, there will be observed forces similar to those arising from heating but opposite in sign, that is, tension on the surface and compression in the middle. In general, then, a temperature gradient established by heating will produce in the outer layers a longitudinal compression, and a gradient established by cooling will cause a longitudinal tension. Such stresses may be called temporary, since they continue only so long as the temperature gradient is maintained. Similarly, if we imagine a temperature gradient to exist in a slab free from stress, the removal of the temperature gradient would cause stresses equal and opposite in sign to those which would be produced by the establishment of the same temperature gradient in a slab originally free from stress. The amount of strain produced by a given temperature gradient depends on the thermal expansion and will be much less for a low-expansion glass, such as silica or Pyrex resistant glass, than for a high-expansion glass, such as common window or bottle glass, or resistant glass of the ordinary types.

The preceding discussion refers to glass at moderate temperatures at which it is elastic. At higher temperatures, however, the glass may flow, and by internal displacement the stresses may gradually be relieved, the rate of release being dependent on the viscosity. At still higher temperatures the stresses may be so evanescent as to escape detection. Suppose that a block of glass initially at a temperature near the softening point is cooled, and in particular that its surface temperature is lowered at a uniform rate. Then the temperature distribution will quickly adjust itself to a parabolic curve, but in this case the establishment of the temperature gradient will not produce any temporary stress, because the glass is too soft

to support stress. Let the glass then, free from stress but containing a temperature gradient, continue to cool at a uniform rate. The temperature gradient will remain practically constant until at some low temperature the cooling is stopped and the temperature throughout the block allowed to equalize. The removal of the temperature gradient will then produce permanent stress, consisting of compression at and near each surface and tension in the middle. If the cooling had been started at an intermediate temperature, such that the temporary stress caused by the establishment of the temperature gradient was not all released, then the remainder of this stress, being opposite in sign to the stress caused by the final removal of the gradient, would partially neutralize the latter, and the permanent stress in the glass would be less than in the first example. From this the conclusion is that the stresses in poorly annealed glass are due to the smoothing out of the temperature gradient at low temperatures, or more exactly, to the part of this effect that is not neutralized by the temporary stress (of opposite sign) carried down from the high temperature. The above statement is equivalent to the following important theorem: The permanent stress is equal and opposite in sign to the stress lost during cooling. This rule has been verified, for cooling glass, by direct continuous observation throughout the entire temperature range and has formed the starting point for a precise treatment of the annealing process.

Adams and Williamson found that at constant temperature, and after a certain length of time, the rate of relief of strain followed the empirical law

$$1/\delta - 1/\delta_0 = A't \quad (1)$$

in which δ and δ_0 are the optical path differences at the time t and the initial time, respectively, and A' is a constant, characteristic of the kind of glass and the temperature. It also was found that the constant A , given by the equation, $A = lA'$ (in which l is the thickness of the

material traversed by the light path), is related to the temperature θ by the equation

$$\log A = M_1\theta - M_2 \quad (2)$$

in which M_1 and M_2 are constants. Table 1 gives the values found by Adams and Williamson for several glasses whose compositions are given in Table 2.

TABLE 1
ANNEALING CONSTANTS AND TEMPERATURES
(After Adams and Williamson)

Values of M_1 and M_2 in the equation $\log A = M_1\theta - M_2$, in which θ is temperature, in degrees Centigrade, and M_1 and M_2 are experimental constants from which may be calculated the annealing constant, A . The annealing temperatures are those at which the strain will fall from 50 to $5\mu\mu$ in the indicated time, as calculated from the formula $At = 1/\Delta n - 1/\Delta n_0$ in which t time is in minutes, Δn , birefringence in $\mu\mu$.

No. in Table 2		M_1	M_2	Annealing Temperatures, Degrees C.						
				2 min.	10 min.	1 hr.	5 hr.	1 day	1 wk.	1 mo.
6	Ordinary crown	0.029	17.35	573	549	522	498	475	446	424
21	Borosilicate crown ..	0.030	18.65	599	575	549	526	503	475	454
36 ca.*	Light Flint	0.033	15.92	461	439	416	395	374	348	329
40 ca.	Light Barium crown ..	0.032	20.10	606	584	559	538	516	490	470
42 ca.	Medium Flint	0.038	18.34	464	445	425	407	389	366	350
44	Barium Flint	0.028	16.28	556	531	503	478	454	424	401
46 ca.	Heavy Flint	0.037	17.51	454	435	414	395	377	354	337
47 ca.	Heavy Barium crown ..	0.038	24.95	638	619	599	580	563	540	524
50 ca.	Extra Heavy Flint ..	0.033	15.03	434	412	389	368	347	321	302

* "ca." indicates that the glass composition is not exactly that given by the authors, but sufficiently close to it for practical purposes.

It will be observed that in Table 1 annealing temperatures are given for several annealing times, calculated from equations 1 and 2, from which it is evident that no one temperature can be considered as the sole annealing temperature. Instead, glass can be annealed over a range of

temperatures, and the one chosen will depend on the conditions. The lower the temperature of annealing the less readily will the glass flow under the temporary strain introduced by a temperature gradient, and the more rapidly it may be safely cooled. The thicker the piece, the more advantageous becomes the lower temperature. Adams and Williamson recommend that glass be annealed at a temperature such that the annealing constant, A , of Table 1 is $0.047/c$, in which c is a factor depending on the expansion coefficient and diffusivity of the glass and on the size and shape of the article, which for slabs of relatively high-expansion glass becomes $13a^2$, a being the semi-thickness.

It is becoming standardized custom to view the annealing of glasses as a viscosity problem. The viscosity of the glass in the annealing zone varies from 10^{13} to $10^{13.4}$ poises depending upon the annealing time used.

3. The Composition of Glass.—The compositions which may be used for technical glassware are limited strictly by the tendency of all glass to devitrify, thus ceasing to be glass, and losing those properties which distinguish glass from other materials. Below a certain temperature range determined by the composition, all commercial silicate glasses are inherently unstable with respect to a crystalline aggregate of the same gross composition. The upper limit of this range is the "liquidus temperature," the temperature at which the first crystals will separate on cooling the glass, or at which the last crystals will dissolve when the devitrified glass is heated, provided always that equilibrium is reached during the operation. Above this temperature the glass cannot devitrify, but if it is held too long in the temperature range immediately below the liquidus, devitrification will take place. The lower limit of the danger range cannot be fixed experimentally, depending as it does not only on the further processes to which the glass is to be subjected but more especially on the interplay of the unknown factors which

determine whether or not a given thermodynamically possible reaction will take place. The liquidus temperature, however, is uniquely fixed by the composition and can be determined experimentally. The relationship between composition and liquidus temperature can be shown best by the detailed consideration of some typical glass-forming systems, and a discussion of these systems will lead to a better understanding of the factors underlying the manufacture of glass.

The Binary System, $Na_2O \cdot SiO_2 - S \cdot O_2$.—The first system to be discussed² is that formed by sodium metasilicate and silica,³ shown in Fig. 2. The vertical scale represents temperature; the horizontal scale, composition. This is part of the larger system, $Na_2O - SiO_2$, and the composition is given in percentage of SiO_2 by weight, considering Na_2O as the other component. The choice of the components in such a case is largely a matter of convenience. Sodium metasilicate, $Na_2O \cdot SiO_2$, and silica, SiO_2 , could as well have been selected as components, and the phase relationships are shown equally well by such a selection. Also, the composition could have been expressed in molecular percentage, using either Na_2O or $Na_2O \cdot SiO_2$ as components; that again is a matter of convenience. Since Na_2O and SiO_2 have molecular weights so nearly equal, their relation as components would give a diagram almost identical with that obtained by the form of representation used in Fig. 2, but if molecular percentages were used with $Na_2O \cdot SiO_2$ and SiO_2 as components the resulting diagram would have appeared distorted because of the high molecular weight of $Na_2O \cdot SiO_2$. Whatever the choice of components, however, the point representing a given composition is the center of gravity when the quantities of the two components corresponding to that composition are placed at the

² For an elementary discussion of phase equilibrium diagrams, see G. W. Morey, *Glass Industry*, **12**, 69 (1931).

³ G. W. Morey and N. L. Bowen, *J. Phys. Chem.*, **28**, 1167 (1924); F. C. Kracek, *J. Phys. Chem.*, **34**, 1583 (1930).

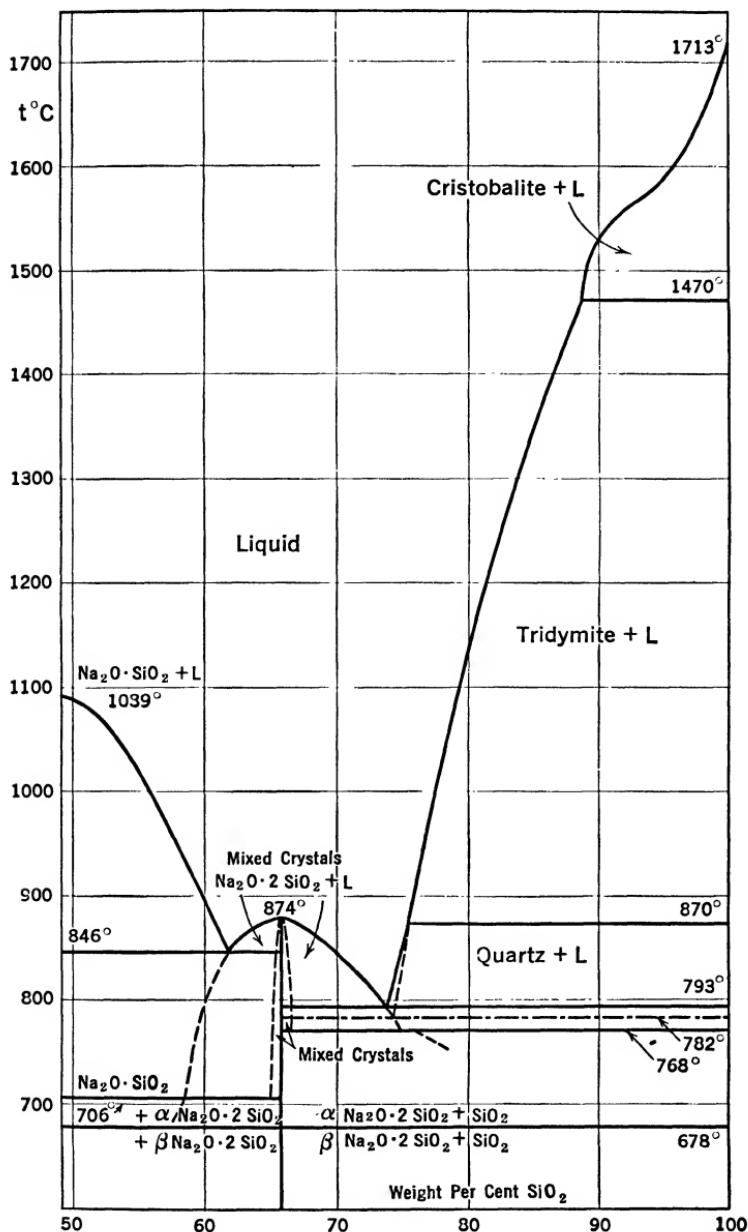


FIG. 2.—Phase Equilibrium Diagram of the Binary System, $\text{Na}_2\text{O} \cdot \text{SiO}_2$. Composition is expressed in weight per cent SiO_2 . After Morey, Bowen and Kracek.

ends of the axis of abscissae. The choice of the method of representation is a matter of convenience; no one method possesses intrinsic superiority over all others.

The region in Fig. 2 inscribed "liquid," above the various freezing-point curves, represents a divariant system, and neither composition nor temperature is fixed by any of the properties under consideration. At a temperature above the liquid and solid curve a whole series of unsaturated liquids may exist, and a given composition may be liquid over a wide range of temperatures. But when a liquid cools to the temperature represented by a freezing-point curve, another phase makes its appearance, and the system loses one degree of freedom. If a liquid containing 80% SiO_2 is cooled, crystals of tridymite, the form of crystalline SiO_2 stable from 870° to 1470°, will separate at about 1135° if given sufficient time. This temperature is uniquely determined by fixing the composition. Only one liquid can coexist with tridymite at 1135°. If a mixture of tridymite and glass, of a gross composition richer in Na_2O than 20%, is held at 1135° the crystals will all dissolve, and the point in the diagram representing that composition at that temperature will be in the divariant field of liquid alone. If the gross composition of the mixture is richer in SiO_2 than 80%, but contains a larger proportion of crystals than corresponds to equilibrium, tridymite will dissolve until the liquid has exactly the composition 20% Na_2O , 80% SiO_2 . The point representing this composition lies within the field "tridymite + liquid," every point of which represents a mixture of these two phases. The composition of the solid phase is constant, that of the liquid changes, as is shown by the freezing-point curve; and the relative proportions of the two phases in any mixture represented by a point in this field are given by the inverse ratio of the length of the portions into which this point divides the horizontal distance from the liquidus to the SiO_2 side of the figure. For example, if the temperature is such that

the liquid contains 78% SiO_2 , and the gross composition of the mixture is 80% SiO_2 , it will consist of 20 parts of liquid and 2 parts of tridymite; while if the gross composition is 98% SiO_2 , the proportions will be 2 parts of liquid, of the same composition as before, and 20 parts of tridymite.

Corresponding to every liquid composition there is a temperature at which it can coexist in equilibrium with crystals. That temperature is called the liquidus temperature. The liquidus curve of a given compound is an example of a univariant system, because fixing either one of the variables, temperature or composition, fixes the other. The intersection of two such univariant curves results in the coexistence of three phases, two solid and one liquid. Such a system is invariant, and both temperature and liquid composition are fixed. This is illustrated by the intersection of the quartz and the sodium disilicate melting-point curves at 793° with a liquid composition of 73.9% SiO_2 . Here the liquid is intermediate in composition between the two solid phases. Whenever the liquid phase can be made up by mixing the two coexisting solid phases the invariant point is a point of minimum temperature for liquid, and is called a eutectic.

Since it is a minimum temperature for liquid, at a eutectic point all liquids freeze completely. A liquid containing 50% SiO_2 will begin to freeze at 1088° ; and as cooling continues, and $\text{Na}_2\text{O}\cdot\text{SiO}_2$ continues to separate, the composition of the liquid will follow the freezing-point curve of sodium metasilicate, until the eutectic is reached. At an intermediate temperature any mixture in the field $\text{Na}_2\text{O}\cdot\text{SiO}_2 + \text{L}$ will be either all liquid, if the temperature is above the liquidus for the composition in question, or a mixture of liquid and $\text{Na}_2\text{O}\cdot\text{SiO}_2$ crystals if below the liquidus. For example, a mixture containing 58% SiO_2 will be all liquid above 955° , at 955° it will begin to crystallize, and at 900° it will be a mixture of

(60–58) parts $\text{Na}_2\text{O}\cdot\text{SiO}_2$ crystals and (58–49.21)⁴ parts liquid. When the eutectic is reached the mixture will consist of (62.1–58) parts of $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ and (58–49.21) parts of eutectic liquid. Then $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ crystallizes out at constant temperature, and the mixture solidifies completely to a mixture of (65.96–58) parts $\text{Na}_2\text{O}\cdot\text{SiO}_2$ and (58–49.21) parts $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$.

The preceding discussion has assumed that equilibrium is reached in all the phase reactions. In the study which established the diagrams every precaution was taken to insure that equilibrium was reached. The persistence of a liquid phase to temperatures below which it is stable, known as undercooling, is not peculiar to glasses, or even to silicates. In considering the properties of glasses or glass-forming systems, it is well to bear in mind that the chemistry of silicates differs not in kind but only in degree from that of the more usual compounds. Those particular compositions of matter which have been found suitable for glasses have the common characteristic that they exhibit a great reluctance to pass from the liquid to the crystalline condition even under the most favorable circumstances, a characteristic often possessed in a less, sometimes even in a greater, degree by many substances wholly unsuitable for use as glass. Many organic substances fall within this category, of which glucose solutions may be taken as an example. Some complex sulphate solutions may be obtained in a glassy form; As_2O_3 and Sb_2O_3 can both be obtained as glass, as can some of their compounds; phosphates are well known as glass formers, and indeed, the so-called meta- and pyro-phosphoric acids probably are known only in the glassy condition; and the oxide B_2O_3 never has been obtained in the crystalline state. Some entirely silicate-free glasses have been articles of commerce. Among silicates, glasses of the composition of the minerals albite and orthoclase are far

⁴ The liquid phase at 900° contains 60% SiO_2 , and the compound $\text{Na}_2\text{O}\cdot\text{SiO}_2$, 49.21% SiO_2 .

more resistant toward crystallization than any commercial glasses. The phenomenon of undercooling commonly occurs with molten salts, and the glasses of commerce represent mixtures in which not only is this property of undercooling to form glasses strongly marked, but in addition the resulting glasses possess other properties which make them useful.

The methods which were used in studying the phase equilibrium relationships in the sodium silicate system are characteristic of those used in all such studies with glass-forming systems and are different from those commonly used in phase equilibrium studies. With salts and metals, the phase transformations may be followed by means of heating or cooling curves. When such materials are heated at a uniform rate an absorption of heat takes place when melting begins which is indicated by the temperature of the charge falling behind that of the furnace, or even remaining constant. Because of the slowness of the melting process in devitrified glasses, as well as in many other silicate mixtures, no indication of the beginning of melting can be found on the heating curves, and indeed the material may even be superheated for a short time many degrees above the temperature of melting without much formation of liquid. This condition is, of course, unstable, and if held above the requisite temperature, the crystals will dissolve, but overheating is the common occurrence. Similarly, on cooling the glass does not freeze—that is why it remains a glass—and hence the type of discontinuity which gives so marked an effect in the freezing of a metal cannot be observed. If held long enough, however, crystals will separate. Accordingly the "quenching" method is used in studying such mixtures. A few milligrams of the material, wrapped in thin platinum or gold foil, are held at a known constant temperature long enough for equilibrium to be reached, which may be a matter of hours, days, or even weeks. Then the charge is cooled in such a manner as to freeze the equi-

librium, and examined with the petrographic microscope; if it is all glass, the temperature of heat treatment was above the liquidus; if a mixture of glass and crystals, it was below the liquidus. By measuring the properties of the crystals they can be positively identified. With difficult mixtures it is customary to have two charges side by side, one initially glass, the other previously crystallized. The heating must be continued long enough for both charges to attain the same condition.

With the exception of compositions near to the disilicate-quartz eutectic there is little difficulty in reaching equilibrium in the $\text{Na}_2\text{O}\cdot\text{SiO}_2\text{--SiO}_2$ system by maintaining the charge at constant temperature, and over most of the composition range an excessive time is not required. On the other hand, glasses of this system undercool to such an extent that the cooling-curve method is not reliable. Sodium disilicate is not difficult to crystallize, at least not in comparison with many commercial glasses; yet until the work of Morey and Bowen thousands of tons of glass of that composition had been made without obtaining the crystalline compound.

Special attention should be called to the $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ -quartz eutectic. There is here a remarkable melting-point lowering; addition of 25% Na_2O lowers the melting point from 1710° to 793° , almost 1000° . Glass of this composition would indeed be excellent were it not that it is easily attacked by water, and hence is not stable in the air. It is of course essential that glass be stable on exposure, not only to the air, but also to far more drastic treatment, and for this reason other oxides must be added. This eutectic is not far from the composition $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$, and the so-called "trisilicate" glasses are usually derived from this eutectic by addition of other oxides, the most important one being lime, CaO . The ternary system which will now be considered consists of sodium metasilicate ($\text{Na}_2\text{O}\cdot\text{SiO}_2$)-calcium metasilicate ($\text{CaO}\cdot\text{SiO}_2$)-silica (SiO_2).

The Ternary System $\text{Na}_2\text{O}\cdot\text{SiO}_2\text{--CaO}\cdot\text{SiO}_2\text{--SiO}_2$.—Details of this system are given in Figs. 3, 4, and 5.

Fig. 3 is a part of the larger equilateral triangle whose vertices represent pure Na_2O , CaO , and SiO_2 . In such an equilateral triangle the point representing a desired composition is the center of gravity of the triangle when loaded at each corner with the proportional quantities of

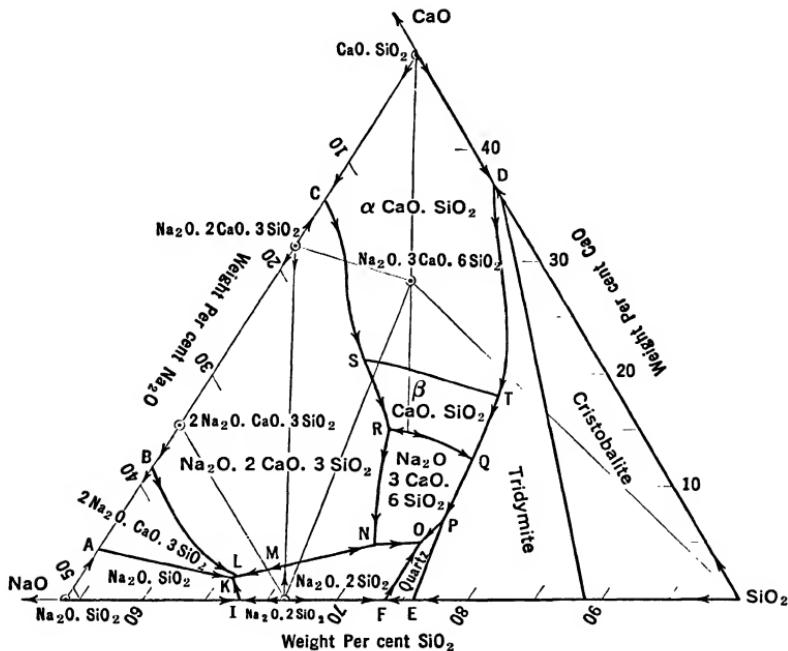


FIG. 3.—Phase Equilibrium Diagram of the Ternary System, $\text{Na}_2\text{O} \cdot \text{SiO}_2 - \text{CaO} \cdot \text{SiO}_2 - \text{SiO}_2$. Composition is expressed in weight per cent of Na_2O , CaO and SiO_2 . After Morey and Bowen.⁵

that component. A point on a side represents a mixture containing only two components, the one represented by the opposite apex being absent; the points on a line through any apex represent mixtures in which the ratio of the other components remains constant; and the points on a line parallel to a side represent mixtures in which the percentage of the component represented by the apex opposite to that side is constant. For example, points on the

⁵ G. W. Morey and N. L. Bowen, Jour. Soc. Glass Tech., 9, 226 (1925); G. W. Morey, J. Amer. Cer. Soc., 13, 683 (1930).

side $\text{Na}_2\text{O}-\text{SiO}_2$ represent the same binary system shown in Fig. 2; points on a line through SiO_2 and the compound $\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 3\text{SiO}_2$ represent mixtures in which the $\text{Na}_2\text{O}:\text{CaO}$ ratio is 1:2; and all mixtures lying on a line parallel to the $\text{Na}_2\text{O}-\text{SiO}_2$ side have the same CaO content. In the figure the scale is indicated on the sides, and may be transferred into the interior of the diagram by coordinate lines parallel to the sides. This method of representing composition in a system of three components has the advantage of symmetry and is more convenient except when one component is present in preponderant amount, as is frequently the case with water and salt systems. In Fig. 4 right-angled coordinates are used in which the weight per cent of SiO_2 is indicated along the horizontal axis, the weight per cent of CaO along the vertical axis, and the weight per cent of Na_2O is obtained by subtracting from 100 the sum of CaO and SiO_2 . This diagram represents the same composition range as that included within the broken lines of Fig. 3 and may be regarded as derived from the rhombus of that figure by means of a shear. The entire diagram of Fig. 3 could be similarly represented by opening out the angle opposite the $\text{CaO}-\text{SiO}_2$ side from 60° to 90° .

Changing the method of representation from weight per cent to mol per cent also would produce a distortion, in amount depending on the differences in the molecular weights of the various components. Either type of diagram can be obtained from the other by the appropriate extension or compression of the different axes, and there is no intrinsic superiority of one type of diagram over the other. It is important to remember that in all such diagrams straight lines remain straight lines. A mixture of $\text{CaO}\cdot\text{SiO}_2$ and $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ remains on the straight line joining these two compounds, no matter whether an equilateral or a right-angled triangle is used, or whether the oxides of any desired binary or ternary compounds are chosen as components, or whether composition is expressed

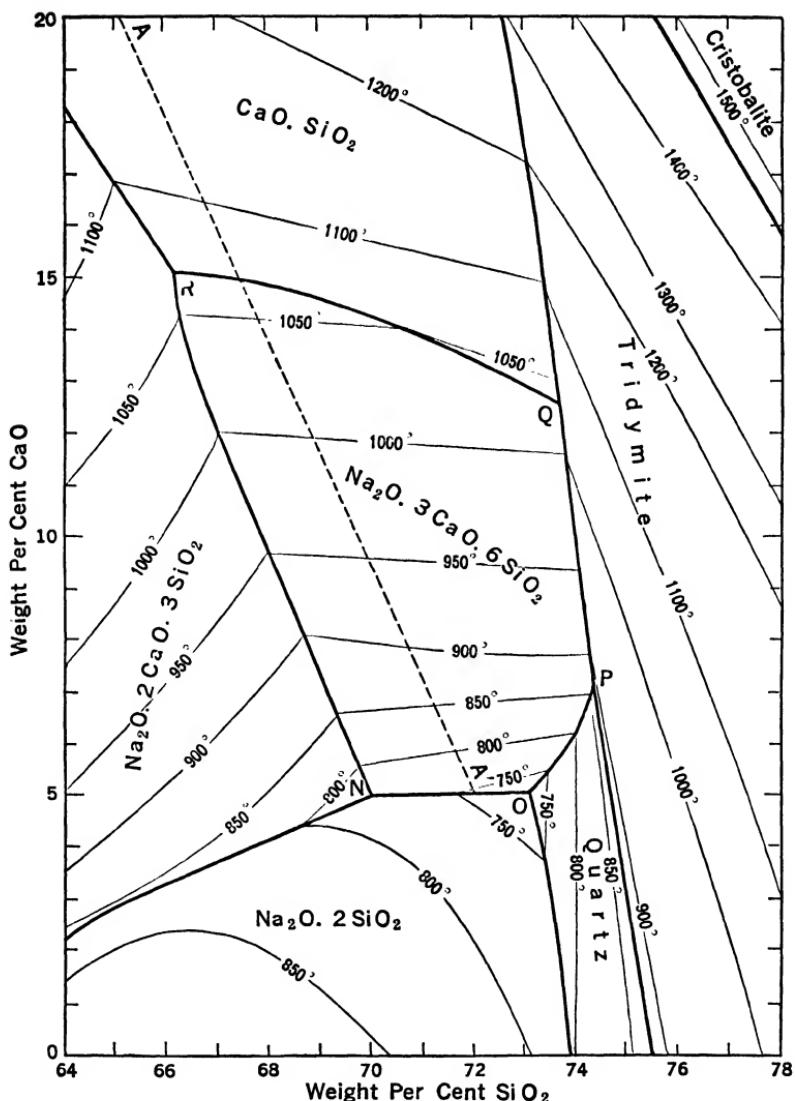


FIG. 4.—The Isotherms and Boundary Lines in the Portion of the Ternary System, $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$, Directly Applicable to Glass Technology. The weight per cent SiO_2 is indicated along the horizontal axis; weight per cent CaO along the vertical axis; weight per cent Na_2O is obtained by subtracting the sum of CaO and SiO_2 from 100. After Morey.

in weight or mol per cent of those oxides or components. Neither is there any virtue in expressing the variation with composition of the physical properties of glass in terms of the percentages of various compounds, even though such compounds may exist in the solid state. One of the characteristics of silicate melts in general, and of those compositions which are used for glass in particular, is that the compounds which separate on crystallization are largely dissociated in the liquid state. The type of dissociation referred to is not an electrolytic dissociation similar to that met with in aqueous solutions, but one more allied to gaseous dissociation, in which molecular complexes suffer rearrangement, and the condition of a glass at a temperature at which its molecules are free to rearrange themselves will probably correspond to transitory groupings containing representatives of all the possible molecular arrangements of the compounds, the relative amounts of the different groupings at any one time being determined by the temperature according to the usual thermodynamic laws. Indeed, it may be that even this vague formulation is too concrete to be in harmony with current views of the constitution of liquids as formulated by the new quantum mechanics.

The complete representation of the three composition variables in a plane is made possible by the additional restriction that their sum must be 100 per cent, thus reducing the independent variables to two. Temperatures must be expressed in a third dimension and is represented by the vertical distance from the base. The equilateral prism thus obtained is terminated by a complex upper surface, representing the liquidus temperatures in the various fields. A photograph of such a model is shown in Fig. 5. If planes parallel to the base be passed through this model at appropriate heights, they will intersect the surfaces in curved lines, giving the composition of the liquids which can coexist with the solid at that temperature, and the isotherms shown in Fig. 4 may be regarded

as the projections of such intersection. The intersection of the surfaces gives rise to the boundary curves of Fig. 3.

Consider now the ternary diagrams, preferably Fig. 3.



FIG. 5.—Sketch of the Solid Composition—Temperature Model Showing Phase Equilibrium Relations in the Ternary System, $\text{Na}_2\text{O}\cdot\text{SiO}_2\text{--CaO}\cdot\text{SiO}_2\text{--SiO}_2$. After Morey and Bowen.

It is divided into several fields by heavy lines, the projections of the valleys between the various mountain slopes of Fig. 5; and the direction of falling temperature along these lines is indicated by arrow-heads. If the various

boundaries are followed to their end it will be found that all mixtures finally come to either one or the other of the two eutectics, to either *K* or *O*. Within each of the fields a different substance is the first to crystallize on cooling, or the last to dissolve on heating. For example, from all mixtures whose compositions lie within the area *BCSRNML*, the compound $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ is the primary phase, and this area is called the field of $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$. As the liquid is cooled and more and more of this compound separates, the composition of the residual liquid changes, and since the crystals and the residual liquid are being formed out of the original liquid, all three compositions must lie on a straight line, with the composition of the original liquid between the other two and dividing the line into segments inversely proportional to the relative amounts of the two phases. This is, of course, the same type of relationship that has already been discussed, with the aid of numerical examples, in the binary system.

As crystallization continues, the composition of the liquid will be continuously displaced on a straight line radiating out from the composition of $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$, until that line intersects one of the boundary curves and the system becomes univariant. With three components at constant pressure, coexistence of two phases produces a divariant system, illustrated by the field of any compound. Divariance in this case means that at any temperature a large number of different liquids may coexist with the solid phase, hence that fixing the temperature does not automatically fix the composition of the liquid. When the system becomes univariant by the appearance of a second crystalline phase, the composition of the liquid becomes fixed when the temperature is fixed, and at any given temperature only one liquid composition can coexist with the two crystalline phases. If the original liquid can be made up of the two crystalline phases that separate at the boundary curve, for example, if it lies on the line joining $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ with $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$, at point *M*,

then it will freeze entirely at this point, and the mixture may be regarded as a binary system within the ternary system, because every reaction that takes place can be expressed in terms of the two end members alone.

The composition of the compound $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ lies within the field of this compound; a liquid of this composition will freeze completely to this compound when cooled, and when the compound is heated it shows a sharp melting point. Such a melting is called congruent. Within the same field is shown the composition of another compound, $2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{SiO}_2$, but the field of this compound is represented by the area *ABLK*. Only from mixtures within this field does $2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{SiO}_2$ crystallize as primary phase. When the pure crystalline compound is heated it remains unchanged until the temperature of the point *B* is reached. Then it begins to decompose into a liquid of the composition *B*, and crystalline $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$; and above this temperature, and at the liquidus, the latter compound is the crystalline phase coexisting with liquid. Such a melting is called incongruent, and the phenomena taking place at this point are entirely analogous to those which take place at the transition point of a salt hydrate.

Of the two ternary compounds already considered, one has an incongruent, the other a congruent, melting point. A third ternary compound is met with in this system, of the composition $\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 6\text{SiO}_2$. This is an extreme case of a compound with an incongruent melting point. The pure compound decomposes at 1060° into liquid and crystals of $\text{CaO} \cdot \text{SiO}_2$, and the melt does not become entirely liquid until 1325° . This compound is characterized by an extreme reluctance to crystallize, and every composition in which it is primary phase is a practical glass composition on a manufacturing scale. Its field is shown in Fig. 3 by the area *NOPQR*, and on a larger scale in Fig. 4, which includes only compositions from 64 to 78% SiO_2 , 0–20% CaO , by weight.

An analysis of the course of crystallization of mixtures

of various compositions will show that all included within the triangle $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ — $\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 6\text{SiO}_2$ — SiO_2 will ultimately solidify completely to a mixture of these three compounds at the ternary eutectic, O , which is at the low temperature of 725° . The part of this region enclosed within the rhombus of Fig. 3 is shown on an enlarged scale in Fig. 4, and on it are indicated isotherms which may be regarded as projections of the intersections of constant-temperature planes with the liquidus surfaces of Fig. 5. This figure includes the compositions of the "soda-lime-silica" group of glasses, which make up by far the greater part of commercial glass production, so far as such glasses can be considered as containing these three components alone. The entire region is dominated by the low-temperature eutectic, which makes the region of commercial-glass compositions one of low temperatures in spite of the high silica content, and at their freezing point they are so viscous that crystallization takes place with extreme difficulty. The temperatures at which the viscosity of these glasses is suitable for the requisite shaping operations are above the liquidus temperature, so that crystallization is impossible; and at the liquidus temperature the crystals which would appear are those of the compound $\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 6\text{SiO}_2$, which is characterized by an extreme reluctance to crystallize. If the composition departs from this narrow range, difficulties begin to appear. If too much SiO_2 is present the liquidus temperature increases rapidly and tridymite separates out with comparative ease. If too much CaO is present the compound $\text{CaO} \cdot \text{SiO}_2$ separates easily, because of both the higher temperature and its greater crystallizing ability. If the glass is in the field of $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$, crystallization takes place still more readily and the glass tends to become too susceptible to decomposition by water. If the glass is in the field of $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$, there is no danger from devitrification, but the glass is easily attacked by water. It is apparent that the range of composition possible for a soda-lime-silica glass is strictly limited to a

small part of Fig. 4, and that the entire diagram is dominated by the low-melting eutectic at *O*. The problem of the glass maker is made easier by the fact that he is never dealing with pure soda-lime-silica glasses but rather with glasses containing small but important amounts of Al_2O_3 , B_2O_3 , and MgO , the effect of each of which is to lower the liquidus temperature and thus to increase the range of feasible glass compositions. In all these glasses, however, the dominant feature is the low liquidus temperature resulting from the low-melting eutectic in the system Na_2O - CaO - SiO_2 .

The Composition of Commercial Glasses.--The first requisite in a commercial glass is that it be not subject to devitrification, and glasses which meet this requirement show a large variation in composition. Most commercial glassware contains silica as its dominant constituent, although this is not necessarily the case, and some silica-free glasses are articles of commerce. In Table 2 are assembled the compositions of a number of typical glasses, including optical and experimental silicate glasses and some silica-free glasses. The silica glasses, however, possess the important quality of superior resistance to weathering, a subject to be discussed later, and silica is the commonest and cheapest of the glass-forming materials. Indeed, silica glass itself possesses in the highest degree the desirable qualities of resistance to weathering and freedom from devitrification, and if it were not so difficult to melt, to obtain free from bubbles, and to work, it would be the most suitable material for most of the uses to which glass is put. However, the cost of manufacture is prohibitive, and other oxides must be added to lower the melting point and decrease the viscosity. In addition, there are some uses in which the modification in the properties of silica obtained by the incorporation of other oxides is essential. The art of the glass maker lies chiefly in the choice and proportioning of the ingredients according to the qualities desired in the finished glass.

TABLE 2
THE COMPOSITIONS OF SOME COMMERCIAL AND EXPERIMENTAL GLASSES

Name	Lit. Ref.	SiO ₂	B ₂ O ₃	Na ₂ O	K ₂ O	CaO	BaO	ZnO	PbO	MgO	Al ₂ O ₃	Fe ₂ O ₃	Mn ₂ O ₃	As ₂ O ₃	
1 Pyrex Chemical Resistant.....	(6)	80.75	12.00	4.10	0.10	0.30	2.20	0.40	
2 (a) Kavalier Combustion.....	(5)	79.57	0.66	11.60	7.80	0.11	0.32	0.04	
3 Libbey.....	(10)	75.9	7.08	6.30	11.0	5.0	0.1	0.3	0.1	0.3	
4 Schott and Gen., Crown.....	O714	74.6	9.0	11.0	5.0	0.1	0.1	0.1	0.3	
5 Winkelmann, Experimental.....	7	(11)	73.8	10.5	7.0	3.0	3.5	0.2	
6 Ordinary Crown.....	(1)	73.1	14.0	1.0	12.0	0.20	0.24	Tr.	Tr.	
7 Schott and Gen., Borosilicate Thermometer, 59 III.....	(9)	72.86	10.43	9.82	0.10	0.35	0.07	0.04	0.01	0	0.2	
8 Schott and Gen., Borosilicate Crown (b).....	O144	(2)	72.15	5.88	5.16	13.85	2.04	0	0	Tr.	0.07	0.04	0.01	0	
9 Schott and Gen., Borosilicate Crown.....	O802	(11)	71.0	14.0	10.0	5.0	
10 Schott and Gen., Zinc Silicate Crown.....	O709	(11)	70.6	17.0	12.0	0.4	
11 Winkelmann, Experimental.....	34	(11)	70.2	12.0	10.3	3.0	4.5	
12 Schott and Gen., Borosilicate Crown (c).....	O3832	(2)	69.58	9.91	8.44	8.37	0.07	2.54	0	0	0.07	0.04	0.01	0	0.22
13 Winkelmann, Experimental.....	90	(8)	69.5	2.0	7.0	16.6	2.5	2.5	0.1	0.4
14 Schott and Gen., Borosilicate Crown.....	O4C	(12)	69.0	2.5	4.0	16.0	8.0	0.1	0.4
15 Bureau of Standards, Light Crown.....	(7)	68.6	3.5	12.0	5.0	9.7	1.0	0.2	0.2	0.2	0.2
16 Schott and Gen., Borosilicate Crown.....	O627	(12)	68.2	10.0	9.5	10.0	9.5	2.0	0.2	0.2	0.2
17 Schott and Gen., Borosilicate Crown.....	O374	(12)	68.1	3.5	5.0	16.0	7.0	0.1	0.3	0.4	0.4
18 Winkelmann, Experimental.....	8	(8)	67.9	16.8	5.8	8.1	1.0	0.1	0.3
19 Schott and Gen., High Dispersion Crown (d).....	O381	(13)	67.40	15.15	1.14	0.39	3.85	10.71	1.72	0.02	0.04	0.14
20 Moncrieff Resistance.....	(3)	67.27	8.89	12.28	1.56	0.86	9.55	0.31
21 Borosilicate Crown.....	(1)	67.0	12.0	9.0	8.0	4.0	0.1	0.4
22 Jena Combustion.....	(5)	66.90	7.22	1.25	2.40	7.94	7.27	0.61	6.38	0.22
23 Jena, Normal Thermometer, 16 III.....	(9)	66.58	0.91	14.80	Tr.	7.18	6.24	0.17	3.84	Tr.	0.28
24 Bureau of Standards, Borosilicate Crown.....	(7)	66.5	7.8	9.8	5.9	7.8	2.0	0.2	0.2	0.2	0.2
25 Jena Gefäße.....	(10)	64.7	10.9	7.5	0.37	0.63	10.9	0.21	4.2	0.25	0.01	0.14
26 Schott and Gen., Silicate Crown.....	O60	(11)	64.6	2.7	5.0	15.0	10.2	2.0	0.1	0.1	0.1	0.4
27 Winkelmann, Experimental.....	3	(8)	64.4	12.0	8.0	11.0	4.5	0.1	0.1	0.1	0.1
28 Schott and Gen., Extra Light Flint.....	O378	(12)	59.3	5.0	8.0	27.5	0.2	0.2	0.2	0.2
29 Bureau of Standards, Barium Flint.....	(7)	58.8	1.7	1.7	8.3	14.3	2.5	12.7	0.3	0.3	0.3
30 Winkelmann, Experimental.....	10	(11)	58.7	33.0	8.0	0.1	0.1	0.1	0.1
31 Winkelmann, Experimental.....	4	(8)	55.0	14.0	14.0	17.0	17.0	0.2	0.2
32 Winkelmann, Experimental.....	32	(11)	54.8	28.0	17.0	0.3	0.3	0.3	0.2	0.2
33 Chance, Fluor Crown (e).....	(4)	54.8	18.7	20.3	0.3	0.3	0.3	0.2	0.2

34	Schott and Gen., Light Flint (<i>f</i>)	(2)	54.75	0.45	4.31	7.99	0.05	1.64	0.96	29.30	0	0.04	0.02	0	0.14
35	Schott and Gen., Borosilicate Crown (<i>g</i>)	O608	(12)	53.5	20.0	6.5	10.1	0.3	39.5	0.2	0.1
36	Chance, Light Flint	1017	(4)	52.8	1.5	9.5	20	7.0	10.0	0.3	0.3
37	<i>•</i> Schott and Gen., Light Barium Flint	O527	(12)	51.7	5.1	25.0	5.0	4.5	0.2	0.2
38	Winkelmann, Experimental	12	(8)	51.3	14.0	0.1
39	Chance, Light Barium Flint (<i>h</i>)	4469	(4)	49.3	3.2	9.5	0.3	27.2	8.6	0.7	0.2	0.1	0.38
40	Schott and Gen., Light Barium Crown (<i>j</i>)	O211	(13)	47.73	3.90	1.14	7.16	0.15	29.88	8.61	0.2	0.65	0.01
41	Bureau of Standards, Barium Crown	(7)	47.6	4.0	2.0	6.0	29.2	9.9	1.4	1.4
42	Chance, Dense Flint	3743	(4)	47.5	5.1	1.2	0.3	45.6	0.2	0.1
43	Chance, Dense Flint	361	(4)	46.3	5.0	1.1	0.3	47.0	0.2	0.1	0.1
44	Barium Flint	(1)	46.0	3.0	4.0	0.1	15.0	8.0	24.0	0.2
45	Winkelmann, Experimental	24	(11)	44.2	0.5	8.0	0.2	47.0	0.1	0.1	0.1	0.2
46	Chance, Extra Dense Flint	337	(4)	40.6	7.5	0.2	51.5	0.2	0.1	0.1
47	Schott and Gen., Heaviest Barium Crown (<i>i</i>)	O1209	(2)	40.17	5.96	0.13	0.03	0.03	42.35	8.17	0	2.79	0.02	0	0.49
48	Chance, Very Dense Flint	4141	(4)	35.1	2.8	0.1	61.8	0.1	0.06	0.25
49	Schott and Gen., Light Borosilicate Flint	O658	(11)	32.75	31.0	1.0	3.0	25.0	7.0	0.2	0.2
50	Schott and Gen., Heavy Silicate Flint	O500	(11)	29.3	3.0	67.5	0.2	0.2
51	Schott and Gen., Heaviest Silicate Flint	S208	(11)	20.0	80.0	0.2	0.2
52	Schott and Gen., Light Borate Crown	S205	(12)	69.1	8.0	4.7	18.0	0.2	0.2
53	Schott and Gen., Zinc Borate	S665	(12)	41.0	59.0
54	Schott and Gen., Light Phosphate Crown	S219	(11)	69.5	3.0	12.0	4.0	10.0	1.5	1.5	1.5
55	Schott and Gen., Phosphate Crown	S206	(11)	59.5	3.0	28.0	8.0	1.5	1.5	1.5

Footnotes

(a) Numbers in italics indicate compositions determined by analysis.

(b) Also: As_2O_3 , 0.08; Cl, 0.06; SO_3 , 0.12; H_2O , 0.08.

(c) Also: As_2O_3 , 0.09; Cl, 0.06; SO_3 , 0.08; H_2O , 0.06.

(d) Also: H_2O , 0.15.

(e) Also: F, 7.5.

(f) Also: As_2O_3 , 0.06; Cl, 0.06; H_2O , 0.20.

(g) Also: Sb_2O_3 , 20.0.

(h) Also: Sb_2O_3 , 0.8.

(i) Also: Cl, 0.03; SO_3 , 0.04; H_2O , 0.14.

(j) Also: As_2O_3 , 0.03.

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(11) Winkelmann and Schott, Ann. Physik, **51**, 697 (1894).

(12) Zschimmer, in Doepler, "Handbuch der Mineralchemie," Leipzig, Steinkopf (1912).

(13) E. Posniak, Analyst, in Wright, "Manufacture of Optical Glass," Ordnance Dept. Document, No. 2037 (1921).

The most widely used glasses are of the "soda-lime" type just considered, consisting essentially of the three oxides, Na_2O , CaO , and SiO_2 , in the proportions determined primarily by the low ternary eutectic in this system. Glass of the composition of this eutectic is too susceptible to the action of water and atmospheric agencies, however, and most soda-lime glasses contain more CaO than corresponds to this eutectic, and in addition small amounts, of the order of 1%, of MgO , Al_2O_3 , or B_2O_3 , or any two, or all of these, added to increase the chemical stability as well as to obtain other desirable qualities. Optical glasses of this type are known as ordinary crowns. They often contain small amounts of B_2O_3 and BaO , and both Na_2O and K_2O may be present. Examples are Nos. 4, 6, 15, and 26 of Table 2. No. 6 is typical of a good quality of plate glass; a sheet glass will usually contain less CaO , and a bottle glass still less.

The so-called "resistance" glasses, with the exception of Pyrex, are modifications of the ordinary crown type, dominated by the same eutectic, but made more resistant to the action of chemical reagents by the addition of other ingredients, usually B_2O_3 , Al_2O_3 , and ZnO , in greater amounts than are used in ordinary "soda-lime" or crown glasses. Nos. 2, 3, 7, 20, 22, 23, and 25 are typical of chemical resistant ware derived from the crown type. No. 2 is excellent for chemical stability, but this and No. 22 are glasses with high softening temperatures, particularly suited for work at high temperatures. Both of these types have been largely superseded by Pyrex chemical resistant ware because of its excellence in both respects.

Pyrex chemical resistant ware,* No. 1 of Table 2, differs from all other types of glass in not being derived in any way

* There is confusion in the literature arising from authors' assuming that "Pyrex" is sufficient to describe the composition of a glass adequately. "Pyrex" is not the name of a material but is a trade mark of the Corning Glass Works covering various thermally, electrically, or chemically resistant glasses of different compositions. The type commonly used for chemical ware is the "Pyrex chemical resistance glass" No. 1 of Table 2, often known by the number G702EJ.

from an alkaline oxide-heavy oxide eutectic, but rather is derived from silica glass by the addition of B_2O_3 and Al_2O_3 with the minimum quantity of alkaline oxide. It is a borosilicate glass but differs in important respects from the older types known by that name. The borosilicate glasses were originally devised for their optical qualities, the presence of B_2O_3 in quantities sufficient to make it a major constituent giving the glass a characteristic lengthening of the red end of the spectrum, which makes them particularly suited to achromatizing the flint glasses in which the relative dispersion in the blue exceeds that in the red. The borosilicates are also low-expansion glasses, although this quality is not marked in many of the optical borosilicates because of the relatively high alkali content. Some borosilicate glasses correspond essentially to the $Na_2O \cdot 2SiO_2$ -quartz eutectic, made stable toward corrosion by the replacement of part of the Na_2O by K_2O and by the addition of an important quantity of B_2O_3 , and also some Al_2O_3 . Examples are Nos. 9, 12, 16, and 25 of Table 2. Other borosilicate crowns contain significant quantities of CaO , or of CaO with either ZnO or BaO , or with both, and may be regarded as combinations of the preceding type with an ordinary crown. Examples are Nos. 7, 8, 14, 17, 21, and 24 of Table 2. No. 7 is the well-known borosilicate thermometer glass, Schott and Gen. 59^{III}. All these glasses contain significant quantities of alkali and are to be regarded as derived from the same dominant eutectic glass in contrast to the Pyrex resistant type previously discussed.

Another important group of glasses comprises the lead glasses or optical flints. These are characterized by the presence of lead oxide in amounts ranging from 20 to 80%, and may be considered as derived from the ternary eutectic in the soda-lime-silica system by the addition of lead metasilicate, with the proviso that as the content of lead oxide is increased the sodium oxide is replaced by potassium oxide. This series of glasses is of great importance in lens design, being used with crowns or borosilicate crowns in achromatic

lenses. In composition they range from the extra light flint (No. 28, Table 2, containing 27.5% PbO), through the dense flints (Nos. 42 and 43, containing 47% PbO), extra dense flints (No. 46, containing 51.5% PbO), very dense flint (No. 48), to the heaviest silicate flint (No. 51, containing 80% PbO). Lead glasses corresponding to the light flints are extensively used for tableware, and the same type was formerly used for blow-pipe work. Lead glasses of about the same or higher lead content have some electrical uses, and glass with much higher lead content is used for X-ray shields.

In all these types there is of course much overlapping, and often the classification of a glass depends on the purpose for which it is used. Many glasses contain both BaO and B₂O₃, yet there are two distinct types of glass containing these oxides, namely the barium crowns, and the barium and the borosilicate flints. These are chiefly of importance for lens design, but variants from them are occasionally met with in special glasses used for other purposes. No. 47 is typical of the dense barium crowns whose use is characteristic of modern high-speed anastigmats, and No. 40 of the light barium crowns. Nos. 37, 39 and 49 illustrate the barium flints and borosilicate flints. Altogether these miscellaneous glasses make evident the wide range in composition possible in glasses which still fulfill the basic requirements of fair freedom from devitrification and resistance to weathering. In Table 2 are also shown a number of experimental glasses, the study of whose physical properties by Winkelmann constitutes our greatest single published source of information as to the properties of glass. Many of them approximate closely to commercial types, and some of them represent silica-free types which have been made commercially, but which cannot be considered successful glasses.

4. The Properties of Glass.—Glass is an engineering material, and as such it is desirable that its properties be known, and that the factors controlling the variation of the properties be determined with enough precision to

make possible the writing of specifications and the control of manufacture. Unfortunately, the science of glass manufacture is too much in its infancy for an adequate treatment of the relation between the various properties and the details of manufacture and composition which determine those properties. Although various properties have been measured, often with high precision, on isolated samples of glass or even on well-selected series of glasses, in but few cases has the composition or history of the glass been known with sufficient accuracy. Many of the data in the literature refer to glasses described in such vague terms as "German glass" or "soft glass." In the following discussion of the properties of glass the sources of the best information are indicated, and an attempt has been made to evaluate the data in the literature critically. Whenever systematic studies have been made of experimental glasses the results are given. In addition, the properties of numerous commercial and experimental polycomponent glasses are given in Table 3.

Since glass is a homogeneous solution consisting largely of SiO_2 together with important but not very different quantities of alkaline oxides, alkaline earth oxides, and trivalent oxides, it is to be expected that the properties of such homogeneous solutions should change in direct proportion to small changes in composition. It has been found that such is the case, and it can be said that many of the properties of glass are roughly additive in character. If they were strictly additive, the numerical values of any property could be calculated from the glass composition and factors representing the value of that property for each pure oxide;

$$P = x_1 p_1 + x_2 p_2 + \dots x_n p_n$$

in which P represents the numerical value of a certain property of a glass containing $x_1, x_2, \dots x_n$ per cent of the components, and $p_1, p_2, \dots p_n$ represents the value of that property for each component. With some properties such

TABLE 3
THE PROPERTIES OF SOME MULTICOMPONENT GLASSES

No. Table 2	Name	Density g./cm. ³	Poisson's Ratio	Young's Modulus	Tensile Strength	Compre- sive Strength	Mean Thermal Expansion $10^6 \frac{\Delta L}{L} \frac{1}{\Delta T}$	Specific Heat g. cal./g. (15-100°)
				(4)	(4)	(4)		
0	Silica glass.....	2.203	0.14	(4)	700	(4) 3-8	0.56 (0-300)	.185 (0-100)
1	Pyrex Chemical Resistant.....	2.25	(1)	611	(1)	3.2 (19-350)	(1) 0.20	(1)
4	Ordinary Crown.....	2.5	(8)	0.221	(5)	644	(6)	
5	Experimental.....	2.479	(7)	717	(6) 0.82	(7) 11.1 (7)	0.196 (6)
7	Borosilicate Thermometer, 59II.....	2.370	(7)	0.210	(5)	711	(6)	
8	Borosilicate Crown.....	2.47	(7)	0.197	(5)	731	(6)	
9	Borosilicate Crown.....	2.370	(7)	0.197	(5)	715	(6) 0.68	(7) 12.4 (7)
10	Zinc Silicate Crown.....	2.572	(7)	0.226	(5)	637	(6) 0.83	(7) 9.6 (7)
11	Experimental.....	2.378	(7)	704	(6) 0.80	(7) 9.7 (7)	
13	Experimental.....	0.221	(5)	621	(6)	
14	Borosilicate Crown.....	2.49	(8)	704	(6)	
16	Borosilicate Crown.....	2.47	(8)	0.213	(5)	781	(6)	
18	Experimental.....	2.629	(8)	651	(6) 0.66	(7) 9.7 (7)	7.97 (17.5-94.7) (3)
23	Normal Thermometer, 16III.....	2.585	(7)	0.228	(6)	732	(6)	8.03 (14.6-92.2) (2)
26	Silicate Crown.....	2.580	(7)	0.231	(5)	647	(6) 0.66	(7) 9.0 (7) 9.63 (17.95.5) (3)

Unit = 1 kilobar
 $= 1.020 \times 10^3 \text{ kg./cm.}^2$
 $= 14.50 \times 10^3 \text{ lb./in.}^2$

27	Experimental.....	2.424	(7)	0.209	(6)
30	Experimental.....	2.518	(7)	0.253	(5)	589	(6) 0.77	(7)	6.7 (7)
31	Experimental.....	2.480	(7)	0.189	(6)
32	Experimental.....	2.668	(7)	0.261	(5)	573	(6) 0.81	(7)	7.2 (7)
34	Light Flint.....	2.6	(8)	0.222	(5)	598	(6)	7.93 (12.9-97.6) (3)
35	Borosilicate Crown.....	2.6	(8)	0.219	(5)
38	Experimental.....	2.848	(7)	709	(6)	4.57 (12.69-89.8) (2) 0.162 (6)
40	Light Barium Crown.....	3.21	(8)	0.252	(5)	727	(6)
45	Experimental.....	3.578	(7)	528	(6) 0.60	(6)	7.6 (7)
46	Extra Dense Flint.....	3.879	(7)	0.224	(5)	535	(6) 0.53	(7)	8.3 (7)
47	Heaviest Barium Crown.....	3.532	(7)	0.271	(5)	783	(6) 0.73	(7)	8.3 (7)
50	Heavy Silicate Flint.....	4.731	(7)	0.239	(5)	537	(6) 0.52	(7)	6.6 (7)
51	Heaviest Silicate Flint.....	5.944	(7)	0.261	(5)	499	(6) 0.35	(7)	5.9 (7) 9.33 (24.5-84) (3)
52	Light Borate Crown.....	2.243	(7)	0.274	(5)	461	(6) 0.57	(7)	8.0 (7) 6.71 (14.4-94.4) (3) 0.218 (6)
53	Zinc Borate.....	3.527	(7)	0.319	(5)	801	(6)	3.33 (10.35-92.9) (3) 0.166 (6)
54	Light Phosphate Crown.....	2.588	(7)	0.235	(5)	664	(6) 0.55	(7)	7.0 (7)
55	Phosphate Crown.....	3.070	(7)	0.253	(5)	620	(6) 0.75	(7)	7.4 (7) 8.70 (20.3-92.2) (3) 0.159 (6)

Literature References

- (1) Corning Glass Works, Corning, New York.
- (2) Hovestadt-Everett, "Jena Glass," New York, Macmillan (1902).
- (3) Pultrich, Ann. Physik, **45**, 609 (1892).
- (4) Sosman, "The Properties of Silica," New York, Chemical Catalog Co. (1927).
- (5) Straubel, Ann. Physik, **68**, 369 (1899).
- (6) Winkelmann, Ann. Physik, **49**, 401 (1893).
- (7) Winkelmann and Schott, Ann. Physik, **51**, 697 (1894).
- (8) Zschimmer, in Doeiter, "Handbuch der Mineralchemie," Leipzig, Steinkopf (1912-).

additive relationships hold within the error of the rather crude measurements by which they may be tested; with others the agreement is very rough indeed.

Weathering.—A valuable property of glass is its resistance to attack by atmospheric agencies; this is of especial importance in its electrical uses. Although many types of glass are so slowly affected as to be practically entirely resistant, all types of glass are essentially unstable with respect to water⁶ so that the distinction between glasses, with respect to this property of weathering, is one of differences between rates of reaction. The various tests applied to glassware to determine its stability with respect to corrosion by the atmosphere are measures of the rate of a reaction under more or less well-defined conditions. The results of such tests should never be expressed as if representing a solubility, for the term solubility has no precise meaning when applied to such measurements. The only unequivocal test is actual service, but it is customary to infer the results of service tests from laboratory measurement, which, when compared with glasses known to be satisfactory and not differing too much from the glass under test, give dependable results.

Weathering tests may be divided into three groups, namely: (1) those in which sensitive methods are used to measure the amount of attack of the glass under standard conditions; (2) those in which the glass is exposed to more or less drastic treatment, differing markedly from any to which it may be subjected in use merely for the purpose of accelerating the reaction; and (3) those in which a combination of both methods is used. The two most important of the first group are the iodeosine method of Mylius⁷ and the method in which powdered glass is extracted with water, and the alkali titrated with standard acid solution. The iodeosine is a colorimetric method of great sensitivity, which in its original form was applied chiefly to fractured

⁶ G. W. Morey, *J. Soc. Glass Tech.*, **6**, 20 (1922).

⁷ F. Mylius, *Silikatzeitschrift*, **1**, 3 (1913); *Glastech. Bericht*, **1**, 33 (1923).

surfaces of known area. It has been used chiefly with optical glass, for which it is well adapted, but it has not met with much success in the general glass field.

The method in which a powdered glass, graded between two sizes of sieves, is extracted with water and the resulting solution titrated with standard acid has many advantages and is probably the best for general use. It requires a carefully standardized procedure, as must of necessity be the case whenever a rate of reaction is being measured, and it is yet to be shown that the results can be duplicated in different laboratories. Moreover, great care must be taken in comparing glasses of different types. The amount of alkali extracted from the glass is a fair basis for comparisons of alkali-lime-silica glasses, or glasses closely related, but the results with such glasses are not to be compared with those of high-lead, high-barium, alkali-free, or borosilicate glasses.

Of the tests in which the rate of reaction is accelerated by drastic treatment the autoclave method is the most widely applied. There is much variation in the details of the method. For results to be comparable it is necessary that the pressure of water and the size and shape of the sample be carefully specified. It is important, too, that it be known whether the sample was completely or partially immersed in liquid at the temperature of the experiment, or if it was exposed to vapor alone. The samples are graded by their appearance, and the test is essentially qualitative in character.

It may be made quantitative by titrating the extracted alkali with standard acid solution. It is doubtful, however, if the apparent increase in precision corresponds to an actual increase in the certainty with which the glasses are graded with respect to the action of atmospheric agencies. Some experimenters have determined the change in weight of the glass resulting from autoclave treatment, but this is uncertain because the glass retains an unknown amount of water and carbon dioxide so that results cannot be checked.

It is generally agreed that the autoclave method is not

a certain way of grading glasses of different types as to how they will stand up under actual service at ordinary temperatures. It is recommended chiefly for comparing glasses of the same type, or for cases where the glass is subjected to high-temperature service. A compromise between the two methods is sometimes used, the powdered glass being extracted with water at an elevated temperature, for example 60° C, and the resulting solution titrated.

Too implicit confidence should not be placed in any one method of testing, and all methods should be used with a full understanding of their limitations. The greatest care must be taken in comparing the results with different types of glass. Tests depending on the liberation of alkali are excellent for comparing glasses of the soda-lime type, but are worthless for comparing such glasses with borosilicates. With this limitation it may be said of all the methods considered that they will discriminate between the definitely bad glasses and the superior glasses; but for the assigning of intermediate grades or for the relative grading of the superior glasses, they lack precision and certainty, and their results are to be accepted with caution.

Density.—The density of glasses ranges from 2.203 for pure SiO_2 to 6.3 for the heaviest lead silicate, and is primarily a function of the composition. The classical study of the relation between the density and composition of glass is that of Winkelmann and Schott,⁸ who worked with complex glasses containing many components. They considered the density to be a purely additive property and gave a series of coefficients by means of which the density of a glass could be calculated from its composition. The assumption of additivity is only roughly true, as can be seen from Fig. 6. In this figure are shown the results of a study by Morey and Merwin⁹ of the density of glasses composed of the three oxides, Na_2O , CaO , and SiO_2 , in widely differing proportions. If the density were truly

⁸ A. Winkelmann and O. Schott, Ann. physik Chem., 51, 697 (1894).

⁹ G. W. Morey and H. E. Merwin, J. Optical Soc. Am., 22, 632 (1932).

additive, the lines of equal density would be a family of equidistant parallel straight lines; but that is not the case. Nevertheless, in the narrow region on this diagram corresponding to commercial glass compositions, the curves do not come far from satisfying these criteria, and the density of ordinary commercial glasses may be considered as very

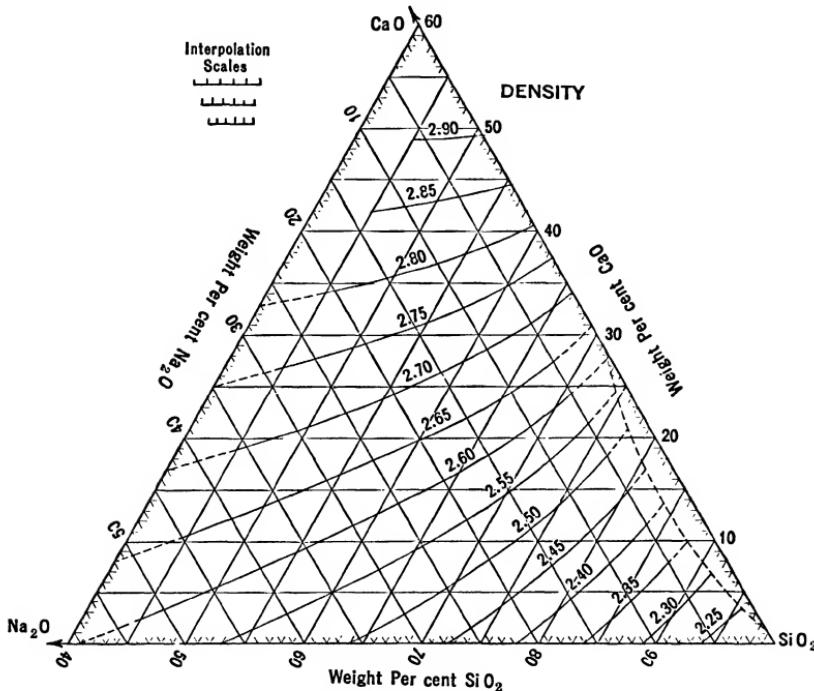


FIG. 6.—The Relationship between Density and Composition in the Ternary System, $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$. After Morey and Merwin.

roughly additive. Factors for the calculation of density from composition have been proposed by several authors¹⁰ since the work of Winkelmann and Schott. The following, proposed by English and Turner, may be the best: SiO_2 , 2.20; Na_2O , 3.47; CaO , 5.00; MgO , 3.38; Al_2O_3 , 2.75;

¹⁰ E. W. Tillotson, *J. Ind. Eng. Chem.*, **4**, 820 (1912); *J. Am. Ceram. Soc.*, **1**, 76 (1918); S. English and W. E. S. Turner, *J. Soc. Glass Tech.*, **6**, 228 (1926); W. L. Baillie, *J. Soc. Chem. Ind.*, **40**, 141 (1921); H. Karmaus, *Sprechsaal*, **59**, 725 (1926).

Fe_2O_3 , 4.0. Another set of factors is given in Table 11 in connection with the thermal conductivity of glass. Gehlhoff and Thomas¹¹ found the calculation of density from composition to be unsatisfactory and suggested instead that the density be calculated from that of a known glass of similar type, certainly a more satisfactory procedure. The discrepancies between the factors proposed by various authors for the same oxide may be illustrated by the factor for CaO , which ranges from 3.3 (Winkelmann and Schott) to 5.0 (English and Turner). In most cases it is better to estimate the density of an unknown glass from that of others of similar type. The densities of numerous commercial glasses are given in Table 3.

Coefficient of Expansion.—The change in density of glass with temperature approximates closely to a linear function of temperature over the range from 0° to 100° C, but more refined measurements require a power series, and as the temperature range is increased, dimensional changes become impossible of representation by any simple type of equation. At the lower temperature, the dimensional changes are reversible, but near the annealing range there may be constitutional changes in the glass, causing apparent erratic variations in the expansion. From this temperature range upward to the melting temperature little experimental work has been done. The recent paper by Hanlein¹² indicates that after glasses have passed through their annealing ranges they follow a normal and regular course of expansion.

In the range from 0° to 100° the coefficient of expansion of glass may be considered as an additive property, within the limits of error of the measurements available. This is illustrated by Fig. 7, in which are plotted the mean linear coefficients of expansions, $\alpha \times 10^6$, from 0° to 90° of a series of glasses of the composition 6SiO_2 , $(2 - x)\text{Na}_2\text{O}$, $x(\text{PbO}, \text{BaO}, \text{CaO}, \text{Al}_2\text{O}_3, \text{ZrO}_2, \text{or MgO})$, obtained by molecular replacement of Na_2O by the oxide in question in a

¹¹ G. Gehlhoff and M. Thomas, *Z. tech. Physik*, **7**, 105 (1926).

¹² W. Hanlein, *Glastech. Ber.*, **10**, 126 (1932).

glass of the composition $2\text{Na}_2\text{O}, 6\text{SiO}_2$. The coefficient of expansion may be calculated on the assumption of additivity by means of the equation

$$3\alpha = a_1p_1 + a_2p_2 + \dots + a_n p_n \quad (3)$$

in which 3α is the cubical coefficient of expansion, p_1, p_2, \dots, p_n the percentages by weight of the various components,

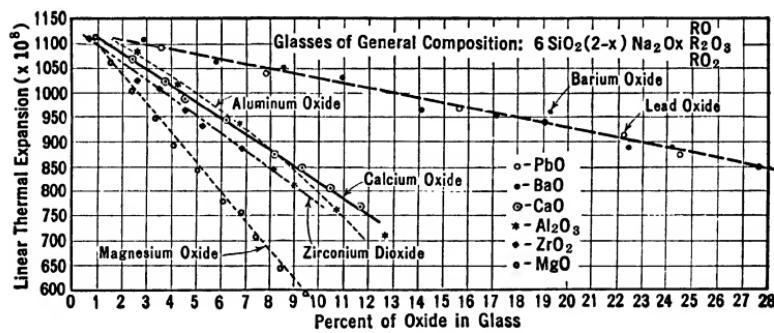


FIG. 7.—The Effect on the Linear Coefficient of Expansion of Replacing Na_2O by the Indicated Percentages of Other Oxides in a Glass of the Composition $2\text{Na}_2\text{O}, 6\text{SiO}_2$. After Turner.

and a_1, a_2, \dots, a_n constants for the various oxides, as given in Table 4.

TABLE 4

FACTORS FOR CALCULATING THE CUBICAL COEFFICIENT OF EXPANSION OF GLASS

Values of a_1, a_2, \dots, a_n in: $3\alpha = a_1p_1 + a_2p_2 + \dots + a_n p_n$, in which p_1 , etc., are the percentages of the given oxides. $\alpha = 10^7\Delta l/\Delta t$.

	English & Turner	Winkelmann & Schott		English & Turner	Winkelmann & Schott
SiO_2	0.15	0.8	BaO	5.2	3.0
B_2O_3	-1.98	0.1	PbO	3.18	3.0
Na_2O	12.96	10.0	ZnO	0.21	1.8
K_2O	11.7	8.5	Al_2O_3	0.52	5.0
CaO	4.89	5.0	ZrO_2	0.69	2.1
MgO	1.35	0.1			

These factors probably will give the coefficient of expansion of a glass of ordinary type to within 5%. The major constituent of most glasses, SiO_2 , is noteworthy as possessing an exceedingly low coefficient of expansion; two other common constituents, Na_2O and K_2O , greatly increase the thermal expansion of glass; and the remaining constituents usually are intermediate between the two. Coefficients of expansion of numerous complex glasses are given in Table 3 and some additional ones in Table 5.

Strength.—The strength of glass is an important engineering factor concerning which our knowledge is in a most unsatisfactory state. There is no consensus of opinion as to the local conditions under which a body is ruptured. It has been assumed that rupture takes place when a maximum tension is reached, or when a maximum extension is reached, or when the difference between the greatest and least stresses reaches a maximum value. Love¹³ summarizes evidence tending to disprove each of these hypotheses, but does not attempt to replace them. The work of Griffith¹⁴ on glass and of Joffé¹⁵ on crystals makes it probable that the true ultimate strength of a material in tension is that determined by the molecular cohesion, and that the far lower values found in practice are caused by surface imperfections. A method has been devised by Littleton¹⁶ for obviating the surface effect, using heat-treated bars whose surface is under high compression while the interior is under tension. When such a bar is broken by bending, the tension introduced in the lower surface is largely neutralized by the initial compression, so that the maximum tension is not in the lower surface but in a zone near the neutral axis. The actual strength is obtained by combining graphically the original stress, as determined from the strain pattern obtained in polarized light, with the load stress. Values so

¹³ A. E. H. Love, "The Mathematical Theory of Elasticity," Cambridge, 1906, Second Edition, p. 119.

¹⁴ A. A. Griffith, *Phil. Trans. Roy. Soc., A*, **221**, 163 (1920).

¹⁵ A. F. Joffé, "The Physics of Crystals," McGraw-Hill, New York, 1928.

¹⁶ J. T. Littleton, *Phys. Rev.*, (2), **22**, 510 (1923).

TABLE 5
MEAN COEFFICIENT OF THERMAL EXPANSION

(See also Table 3) $l = l_0 (1 + 10^{-6} \alpha t)$

No. in Table 2	α	Range, Degrees C.	Literature Reference	No. in Table 2	α	Range, Degrees C	Literature Reference
15	10.2 55.5	22-426 502-522	(2)	37	9.00	10-93	(1)
17	9.12	18-97	(1)	39	7.74		(5)
19	9.03	16-94	(1)	54 ca.	7.88	11-99	(4)
23	See Below	-253-100	(3)	56	9.00	23-499	(2)
24	9.00 39.3	22-498 539-562	(2)	64.9	64.9	569-610	
24	9.00 39.3	22-498 539-562	(2)	67 ca.	8.33		(5)
26	9.20 10.04 10.61 11.11	37 (mean) 93 (mean) 151 (mean) 212 (mean)	(1)	68	5.23	7-92	(4)
26	9.20 10.04 10.61 11.11	37 (mean) 93 (mean) 151 (mean) 212 (mean)	(1)	70 ca.	8.03	20-94	(1)
28	8.14		(5)	71 ca.	9.34	18-99	(4)
28	8.14		(5)	74 ca.	9.30	18-93	(1)
29	8.8 33.1	22-494 519-550	(2)	75	8.71	21-100	(4)
36 ca. *	8.8 34.7	22-451 494-512	(2)	23	$1 = 1_0 \{ 1 + 10^{-6} [716.8(t/100) + 48.33(t/100)^2 + 9.02(t/100)^3 + 10.9(t/100)^4] \}$		

* "ca." indicates that the glass composition is not that given by the authors, but sufficiently close to it for practical purposes.

Literature References

- (1) Hovestadt-Everett, "Jena Glass," New York, Macmillan (1902).
- (2) Peters and Cragoe, Bur. Standards Sci. Paper 393 (1920).
- (3) van Agt and Onnes, Verslag K. Akad. Wetenschappen Amsterdam, **34**, 618 (1925).
- (4) Pulfrich, Ann. Physik, **45**, 609 (1892).
- (5) Zschimmer, Silikat-Z., **2**, 129 (1914).

obtained were found to be greater than those obtained by the usual methods. Milligan¹⁷ found that the strength of glass containing cracks is greatly influenced by the medium in contact with the glass surface, and it is well known that the apparent strength can be increased by light etching with hydrofluoric acid. It is probable, therefore, that the values which have been obtained for the strength of glass have been determined by the condition of the surface, and that the true ultimate strength of glass is not realizable in practice.

Other factors greatly influence the value experimentally found for the strength of glass. Numerous observers have found the strength per unit area to decrease with increase in size, and glass fibers will ordinarily have many times the strength of the same glass in more massive form. The duration of the load also is important. For example, Grenet¹⁸ found the breaking strength, in kilobars (compare Table 3), of strips of glass loaded in the middle; after 1 sec, 0.72; 40 min, 0.47; 2 hours, 0.42; 40 hours, 0.33; in a second series of experiments in which the load was left on until the piece broke, it was found that with a load of 0.3 kilobar the piece broke after 2 days; with 0.25, after 3 months; and 0.20 kilobar did not break the piece in 4 months. The results of such experiments would depend considerably upon the local vibration conditions. The homogeneity of the glass may have an important bearing on the observed strength, particularly as the presence of heterogeneities may determine the occurrence of local strains or flaws and thus cause early fracture. The effect of strain itself is important, as is shown by the method of Littleton, mentioned above, for the better determination of the strength of glass, and glass can be greatly strengthened¹⁹ by producing a strongly compressed surface layer.

¹⁷ L. H. Milligan, *J. Soc. Glass Tech.*, **13**, 351 (1929).

¹⁸ Grenet, *Bul. Soc. Encouragement*, 839 (1899). Cited by LeChatelier, "La silice et les silicates," A. Hermann et Fils, Paris, p. 308 (1914).

¹⁹ J. T. Littleton and F. W. Preston, *J. Soc. Glass Tech.*, **13**, 336 (1929).

Littleton and Preston state that by proper heat treatment it is possible to increase the tensile strength of rods or bars by 50%, and the bending strength by at least 150%, with a theoretical limit of 230%.

The classic study of the strength of glass is that of Winkelmann and Schott,²⁰ and the values in Table 3 of the tensile and compressive strength of a number of glasses are taken from their work. The values given for the tensile strength represent the maximum obtained. The minimum values were from 4% to 22% lower. Winkelmann and Schott used rods on each of which a shallow depression was made by grinding, and afterwards polished. In view of the considerations given above it is probable that flaws or cracks produced in the grinding operation determined the strength obtained. In the compressive tests, cubes 6 mm on an edge were squeezed between two metal plates until they flew to powder. The relation between tensile strength and crushing strength, shown in Table 3, is that commonly observed, namely about 1 : 12, with a range from 1 : 9 to 1 : 18. The value obtained for crushing strength depends in a large measure on the precision with which the press is set up and on the material of the plates. The results of Winkelmann and Schott give values for their glass 19 of 55,800 lb per sq in. when tested between block tin plates, 94,000 lb per sq in. between copper plates, and 179,000 lb per sq in. between hardened steel plates. This shows that to obtain the highest strengths hardened metals should be used. The softer metals flow parallel to the surface of the glass and introduce a tearing action. In commercial practice, however, it is not generally practicable to use a ground and polished surface contact. Therefore the hardened metals tend to localize the pressures on their points of contact, and hence the softer metals are found to give better results. The soft metals equalize the pressure distribution, owing to the fact that they flow. By the use of a soft metal, assemblies having a theoretical crushing strength of 50,000

²⁰ A. Winkelmann and O. Schott, Ann. physik. Chem., 51, 697 (1894).

lb per sq in. should be readily obtainable in practical applications.

Winkelmann and Schott give factors for calculating the strength from the composition which agree with their results to within about the same percentage of deviation as the agreement of the observations among themselves, that is to about 25%, but do not agree with the results of other observers.

Kowalski²¹ compared the strength in tension, flexure, torsion, and compression of a glass of unknown composition, and also calculated the maximum extension with the various types of load. The results are assembled in Table 6. These results indicate that glass can bear a considerably greater extension by torsion than by pull or bending or end pressure. As there is no generally accepted theory of the conditions under which a body is ruptured, there is no necessary connection between the strengths under these various types of load.

TABLE 6

COMPARISON OF THE STRENGTH OF GLASS UNDER VARIOUS TYPES OF LOAD,
AND OF THE MAXIMUM EXTENSION

(After Kowalski)

	Strength in Kilobars (1 Kilobar = 1.45×10^4 Pounds per Square Inch)	Maximum Extension
Tension	0.86	0.00131
Flexure	0.86	0.00132
Torsion	0.99	0.00183
Compression	3.70	0.00129

Although the true strength of glass is never attained because of the effect of surface imperfections, experience has shown that a tensile strength of approximately 0.7 kilobar (10,000 lb per sq in.) is a fair estimate of the strength

²¹ J. V. Kowalski, Ann. Physik, **36**, 307 (1889).

to be expected, although greater values are frequently found. In general engineering calculations, however, a factor of safety of 4 or 5 should be allowed when this value of the tensile strength is used.

Several experimenters have determined the bursting strength of glass tubes. None of them gives the composition of the glass used, but as the experiments of Onnes and Braak ²² are the most extensive they will be discussed. The samples used were described as ordinary Thuringian glass. Three groups of experiments were made: (1) with thick-walled tubes of large diameter; (2) with thick-walled tubes of small internal diameter, i.e., capillary tubes; and (3) with thin-walled tubes of large bore. The data were reduced to a comparable basis by calculating the maximum fiber stress from the formula

$$T_m = 1/4 \{ 5P_m + 7[(P_m - 1)/((R/R')^2 - 1)] - 1 \} \quad (4)$$

in which T_m is the maximum fiber stress, P_m is the bursting pressure, and R and R' are the external and internal radii, respectively. The results are summarized in Table 7. It

TABLE 7
BURSTING STRENGTH OF GLASS TUBES
(After Onnes and Braak)

Maximum fiber stress, T_m , calculated from formula (4)

Unit = 1 bar = 1.020 kg per cm² = 14.50 lb per in.²

Shape of Tubes	Range of Radii, mm		Number of Tubes Tested	Range of Bursting Pressures	Maximum Fiber Stress	Mean Variation from Mean Per Cent
	External R	Internal R'				
Thick-walled	0.0-18.0	3.00-6.0	9	230-380	470	14
Capillary	5.0-7.0	0.24-1.0	16	420-1200	902	27
Thin-walled	3.8-7.8	3.4-7.3	17	54-377	628	20

²² K. Onnes and Braak, *Verslag Akad. Wetenschappen Amsterdam*, **16**, 890 (1907-8).

will be observed that the results are irregular, and that the maximum fiber stresses obtained were less than the same investigators found for fibers made from the same glass.

Little is known about the effect of temperature upon the strength of glass. At ordinary temperatures, glass is devoid of plasticity, and there is no evidence that with increased temperature a region of plasticity develops. As the temperature is increased, the diminution of viscosity makes the strength evanescent for loads of a duration decreasing with increasing temperature. This is illustrated by the results obtained by Laubengayer²³ on the collapsing temperatures of glass tubes of 13-mm bore and 1.8-mm wall thickness, heated at 3° C per minute, either open to the air or evacuated to 3-mm pressure. The results are assembled in Table 8.

TABLE 8
COLLAPSING TEMPERATURES OF GLASS TUBES, DEGREES C.
(After Laubengayer)

	Open	Evacuated
Soft soda-lime, Greiner and Fredericks.....	700	585
Resistance, Greiner and Fredericks.....	750	635
Pyrex, Corning Glass Works *	820	670
Bohemian Combustion.....	860	740
Moncrieff Combustion.....	820	770

* This probably refers to Pyrex chemical resistant glass.

Brittleness.—Brittleness is a term descriptive of the tendency of some substances to break or shatter when subjected to stresses exceeding the elastic limit, in contrast to the gradual and continuous deformation of a plastic substance under similar conditions. The term usually implies a shattering under sudden stress and does not admit of precise definition or measurement. It usually is considered

²³ A. W. Laubengayer, Ind. Eng. Chem., **21**, 174 (1929); Glass, **6**, 111 (1929).

to be measured by the impact strength, or the energy required to destroy by impact, but there is no agreement as to the calculation of the quantity from the experimental data. Preston²⁴ discussed various formulae and showed that the correct statement of the usual formulation resulted in a quantity directly comparable with the tensile strength. A comparison of some experimental results showed the tensile strength computed from impact data to average 1.42 times the tensile strength as measured by other methods, and some such ratio probably will generally be found to hold.

Elasticity.—When a piece of glass is strained by an applied force the glass returns to its original size and shape on removal of the force, provided that the temperature is not too high, and that the force is neither too great nor applied for too long a time. The property by which the glass regains its original dimensions is called elasticity and is measured by the ratio of the stress to the strain. The stress may be applied in various ways, for example by hydrostatic pressure, producing a pure compression in which the elasticity is measured by the bulk modulus, K ; by torsion, producing a shear, in which case the elasticity is measured by the modulus of rigidity, R ; or by bending or tension, both of which produce both compression and shear. The modulus of extension in tension is known as Young's modulus, E , which is related to the other elastic constants by the equations

$$E = 9KR/(3K + R) = 3K(1 - 2\sigma) = 2R(1 + \sigma) \quad (5)$$

in which σ is Poisson's ratio, the ratio of lateral to longitudinal strain under unidirectional stress. By these equations, the values of any two of these four interrelated quantities can be calculated if the other two are known.

The elasticity of glass at ordinary temperatures is a function of its composition, but the relationship has not been adequately studied. The elastic constants of silica

²⁴ F. W. Preston, J. Am. Ceram. Soc., **14**, 428 (1931).

glass have been discussed by Sosman²⁵ and are given in Table 3. Clarke and Turner²⁶ measured Young's modulus of a linear series of glasses in the ternary system $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$, derived from a glass of the composition Na_2O , 3SiO_2 by the molecular replacement of Na_2O by CaO , with CaO contents ranging from 0 to 12% by weight. Their results are represented by the formula $E = 13.9y + 565.6$, in which E = Young's modulus in kilobars, y = weight per cent CaO .

Gehlhoff and Thomas²⁷ determined Young's modulus for a series of glasses derived from a glass containing 18% Na_2O , 82% SiO_2 by weight, by replacing SiO_2 with one of the oxides Na_2O , K_2O , MgO , CaO , ZnO , BaO , PbO , B_2O_3 , Al_2O_3 , or Fe_2O_3 . The results are given in a series of diagrams which are reproduced in Fig. 8. Replacing SiO_2 by either Na_2O or K_2O results in a decrease in elasticity, and replacing Na_2O by K_2O results in a slightly increased elasticity. All other oxides increased the elasticity, although PbO had but little effect. The curve for B_2O_3 passes through a well-marked maximum, and it is probable that the curve for Al_2O_3 has a similar shape.

Most of the data in the literature pertain to commercial glasses containing from four to eight or more components and are of value only in respect to the piece of glass measured. Sufficient examples are given in Table 3 to indicate the approximate value of the elastic constants for any given type of glass. These glasses are too complicated and the data are too scanty to permit the assignment of any particular part of the elasticity to any one component, and the calculation of an elastic constant by means of the various empirical factors which have been proposed is too uncertain to justify the inclusion of such factors.

The effect of temperature on elasticity is a difficult problem which has been attacked by few investigators.

²⁵ R. B. Sosman, "The Properties of Silica," Chemical Catalog Co., (1927).

²⁶ J. R. Clarke and W. E. S. Turner, J. Soc. Glass Tech., 3, 260 (1919).

²⁷ G. Gehlhoff and M. Thomas, Z. tech. Physik, 7, 105 (1926).

Winkelmann²⁸ made the only extended contribution to the subject. He found that at temperatures from 340° to 480°, depending on the composition of the glass, the deflection for a given load increased rapidly as the load was left on, and it was necessary to take readings immediately after loading. Although at these temperatures glass is elastic

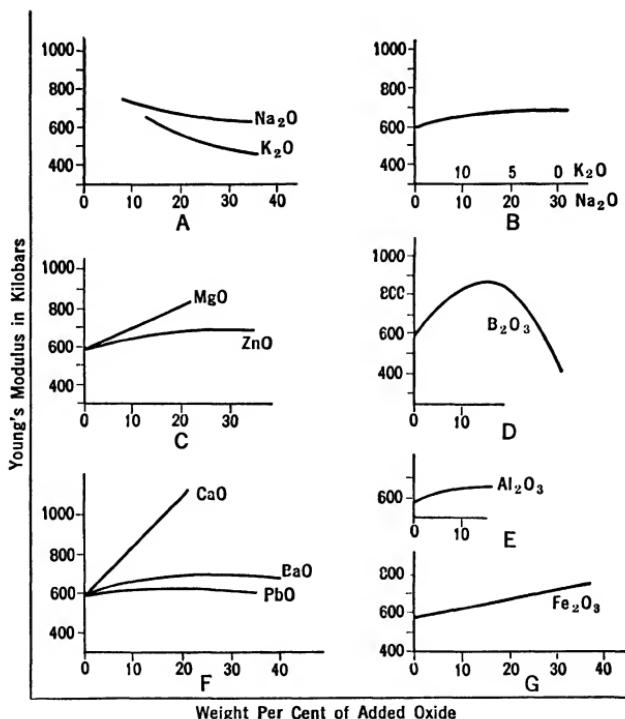


FIG. 8.—The Effect on Young's Modulus of a Glass 0.18 Na₂O, 0.82 SiO₂, of Replacing SiO₂ by the Indicated Weight Per Cent of Other Oxides. After Gehlhoff and Thomas.

to loads of short duration, it is actually a liquid of high viscosity and flows slowly under load. Winkelmann further found that the elasticity was greatly affected by the previous thermal history of the glass. When the change in dimensions of the test piece with temperature was ignored

²⁸ A. Winkelmann and O. Schott, Ann. physik. Chem., 51, 697 (1894).

in the calculation, Young's modulus decreased with temperature, but when this correction was applied the "true" elasticity was found to be independent of temperature. The effect of lack of annealing is to diminish the elasticity.

Specific Heat.—Specific heat is generally assumed to be approximately additive, both for crystals and for liquid mixtures, although it is well known that precise measurements show departures from the additive relation. The specific heat of glass also is approximately additive, as is shown by the results of Winkelmann,²⁹ who measured the specific heat, in the temperature zone of approximately 0° to 100° C, of a number of glasses whose compositions were not accurately known, and obtained results which agreed to within 1 to 2% of those calculated from the composition, using the factors for the several oxides given in Table 9. These are mostly the factors previously published by Regnault,³⁰ deduced from measurements on crystalline compounds. A real study of the specific heat of glass is greatly to be desired.

TABLE 9
FACTORS FOR THE CALCULATION OF SPECIFIC HEAT
(After Winkelmann)

SiO ₂	0.1913	CaO.....	0.1903
B ₂ O ₃	0.2272	BaO.....	0.0673
P ₂ O ₅	0.1902	ZnO.....	0.1248
Na ₂ O.....	0.2674	PbO.....	0.0512
K ₂ O.....	0.1860	MgO.....	0.2439
Li ₂ O.....	0.5497	Al ₂ O ₃	0.2074

DeVries³¹ determined the specific heat of Pyrex resistant laboratory ware by the Nernst method from 25° to 175° C and found his experimental results to be well represented by the formula

$$\text{Specific heat} = 0.1839 + 0.0003134 (t - 20^\circ \text{ C}).$$

²⁹ Winkelmann, Ann. physik. Chem., **49**, 401 (1893).

³⁰ Regnault, Ann. chim. phys., **1**, 129 (1841).

³¹ Thos. DeVries, Ind. Eng. Chem., **22**, 617 (1930).

The specific heats of some commercial and experimental glasses are given in Table 3.

Thermal Conductivity.—Like specific heat, the thermal conductivity is considered to be additive, but the experimental data are not sufficient to confirm the assumption. Paalhorn³² measured the thermal conductivity of a number of the glasses studied by Winkelmann and proposed factors for the calculation of conductivity from composition which agreed fairly well with his observed values. Later, Focke,³³ working with similar glasses, obtained results differing by as much as 40% from those of Paalhorn and proposed new factors. Probably the best work is that of Euchen,³⁴ who determined the thermal conductivity of a number of optical glasses. His results are reproduced in Table 10. Russ,³⁵ a pupil of Euchen, measured the thermal

TABLE 10
THERMAL CONDUCTIVITY
(After Euchen)

No. in Table 2	$10^{-3} \text{ g-cal cm}^{-2} \text{ sec}^{-1} (\text{ }^\circ \text{C, cm}^{-1})^{-1}$			
	-190°	-78°	0°	100°
9	1.181	2.532	2.796	3.243
12	1.195	2.825	
43 ca. *	0.865	1.900	
46 ca.	0.807	1.698	1.812
53	0.877	1.796	2.007

* "ca." indicates that the glass composition is not that given by the author but sufficiently close to it for practical purposes.

conductivity of the various series of glasses prepared by Gehlhoff and Thomas (cf. p. 48). Neither the commercial

³² O. Paalhorn, Diss., Jena, 1894. Quoted in "Jena Glass," H. Hovestadt, translated by J. D. and A. Everett, Macmillan, 1902.

³³ Focke, Ann. physik. Chem., **67**, 132-159 (1899).

³⁴ A. Eucken, Ann. Physik, **34**, 185 (1911).

³⁵ A. Russ, Sprechsaal, **61**, 887, 907 (1928).

glasses used by Euchen nor the experimental glasses used by Russ were analyzed, and the correlation between the observed values of heat conductivity and those calculated on the basis of an additive relationship cannot be close. Russ, following Winkelmann,³⁶ calculates thermal conductivity from composition by the formula

$$1/\lambda = b_1/\lambda_1 + b_2/\lambda_2 + \dots b_n/\lambda_n \quad (6)$$

in which λ is the reciprocal of the thermal conductivity; and $\lambda_1, \lambda_2, \dots \lambda_n$ constants for the various components whose percentages by volume are given by $b_1, b_2, \dots b_n$. Values of constants for the various oxides are given in Table 11 together with the factors for density used by Russ.

TABLE 11

FACTORS FOR THE CALCULATION OF THERMAL CONDUCTIVITY
(After Russ)

Oxide	Density Factor	Thermal Conductivity Factor	Oxide	Density Factor	Thermal Conductivity Factor
SiO ₂	2.30	3.00	ZnO	5.90	8.65
B ₂ O ₃	2.35	3.70	PbO	10.00	11.70
Na ₂ O	3.20	10.70	MgO	3.90	4.55
K ₂ O	2.90	13.40	Al ₂ O ₃	3.20	6.25
CaO	3.90	8.80	Fe ₂ O ₃	3.87	
BaO	7.10	11.85			

The volume percentages were calculated from the assumed compositions of the glasses by means of these density factors, and the agreement between observed and calculated results ranged from -6.5 to +7.8%. More precise studies of the thermal conductivity, using glasses of known composition and properties, are greatly to be desired.

Experiments³⁷ on the heat transfer through tubular

³⁶ A. Winkelmann, Ann. physik. Chem., **67**, 794 (1899).

³⁷ J. T. Littleton, Jr., and H. C. Bates, Trans. Am. Inst. Chem. Eng., **17**, 95 (1925); Chem. Met. Eng., **39**, 315 (1932).

heaters of glass and of metal lead to the conclusion that with glass tubes the low volume conductivity reduces the total heat transfer, but to a much smaller extent than would be expected. Clean copper, with a thermal conductivity coefficient 300 times that of glass, condenses only 2.5 times as much steam, and a slight corrosion film reduces this considerably. This result is what would have been anticipated, as it is known that in certain cases where film resistances are high the thickness of the material and its volume conductivity are not very important.

Resistance to Thermal Shock.—The resistance of glass-ware to thermal shock is a complex quality, whose specification and measurement present formidable difficulties. Winkelmann and Schott³⁸ defined the coefficient of thermal endurance by the expression

$$F = [T/(\alpha E)] [K/(cd)]^{1/2},$$

in which T is the tensile strength; E , Young's modulus; α , linear coefficient of thermal expansion; K , the thermal conductivity; d , the density; and c , the specific heat. Stott,³⁹ by dimensional analysis, deduced a relation for the temperature difference required to cause breakage, $\theta - \theta_c$, which for a sphere reduces to

$$(\theta - \theta_c) \propto [T(1 - \sigma)] / (E\alpha) \quad (8)$$

in which T is tensile strength; E , Young's modulus; σ , Poisson's ratio; and α , linear coefficient of thermal expansion. This formula does not contain the thermal diffusivity, the inclusion of which in the formula of Winkelmann and Schott is ascribed to fallacious reasoning. In both these formulae the measure of resistance varies inversely as the coefficient of expansion, and it is doubtful if the use of these formulae in comparing various glasses offers any advantage over the comparison of expansion coefficients alone. The coefficient of expansion is more affected by differences of

³⁸ A. Winkelmann and O. Schott, Ann. physik. Chem., 51, 730 (1894).

³⁹ V. H. Stott, J. Soc. Glass Tech., 8, 139 (1924).

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composition than is Young's modulus, Poisson's ratio, or the tensile strength. Moreover, since the tensile strength is largely determined by surface conditions, the breakage of glasses of similar expansion properties under thermal shock will be determined largely by the condition of their surfaces. This fact is the explanation of the greater thermal resistance of "toughened" glass and also of the erratic results usually obtained in carrying out tests of this property. Such tests are usually made by filling flasks or beakers with paraffin oil, heating to successively increasing temperatures, and plunging into ice water. Various types of chemical resistant glasses will withstand from 150° to 250° C change in temperature when tested according to this method, the actual value depending on the type of glass. Well-annealed glass is inferior in thermal endurance to glass in which the surface layers are in compression because of strain, and in toughened glass such a strain is deliberately produced.

CHAPTER II

ELECTRICAL CONDUCTIVITY OF GLASS

1. Definitions.—The electrical conductivity of glass depends on the composition, on the temperature, and to some extent on the surrounding atmospheric conditions. At low temperatures, polycomponent glasses are insulators, and some are among the best insulating substances. At all temperatures, glasses are electrolytic conductors, and from 25° to 1200° C, the resistivity range may be from 10^{19} ohms to 1 ohm.

The measurement of volume conductivity at low temperatures is complicated by the surface conductivity, which is probably caused by a layer of adsorbed moisture, and which is particularly troublesome at high humidity and with glasses high in alkali, and may amount to many times the volume conductivity.

The volume resistivity is defined as the longitudinal resistance in ohms per unit of length of a uniform bar of unit sectional area; the volume conductivity is the reciprocal of the resistivity.

The surface resistivity is usually defined as the resistance in ohms of a strip of the surface of unit length and width.

2. Mechanism.—Many studies of the conduction of electricity through glass have been undertaken to secure knowledge of the mechanism of this process. The early work of Buff¹ and of Beetz² was followed by the classic work of Warburg,³ and its extension by Warburg and

¹ H. Buff, Lieb. Ann., **110**, 257 (1859).

² W. Beetz, Ann. physik. Chem., Jubelband, p. 23 (1874).

³ E. Warburg, Ann. physik. Chem., **21**, 622 (1884).

Tegetmeier⁴ and by Tegetmeier.⁵ Warburg established the basic fact of the electrolytic nature of the conductivity, which he found to take place in accordance with Faraday's law. He used test tubes of Thuringian glass, filled with mercury or sodium amalgam and immersed in a similar bath, heated usually to 500° C. The mercury or amalgam inside and outside of the test tube served as electrodes. With mercury electrodes, the conductivity rapidly diminished as electrolysis continued, falling to one-thousandth of its initial value in a hour. This decline was ascribed to the decrease in sodium content at the anode, which decrease was prevented by the use of sodium amalgam electrodes. With sodium amalgam electrodes, sodium was transported through the glass. Warburg and Tegetmeier showed that the conductivity of crystalline quartz is caused by the presence of sodium; later studies have failed to show whether the sodium is present as chloride, oxide, or silicate, and the mechanism of the conduction⁶ is still an open question. Tegetmeier found that, although the glass used by Warburg conducted with a sodium amalgam electrode, it did not do so with potassium amalgam. With lithium amalgam the glass conducted, with replacement of sodium by lithium, and formation of an opaque glass, which quickly shattered. Attempts to electrolyze with Ca, Mg, Al, Zn, Bi, and Au amalgam electrodes failed; the conductivity dropped immediately to zero, and there was no transfer of metallic ions into the glass. He also showed that only a portion of the sodium ions in the glass took part in the conduction process. LeBlanc and Kerschbaum⁷ showed that the glass could be restored to its original condition by electrolytic replacement of sodium in the anode layer, or by grinding off the anode layer. They also showed that when the anode layer was heated oxygen was evolved, in

⁴ E. Warburg and F. Tegetmeier, *Ann. physik. Chem.*, **35**, 455 (1888).

⁵ F. Tegetmeier, *Ann. physik. Chem.*, **41**, 18 (1890).

⁶ See A. Joffé, "The Physics of Crystals," McGraw Hill Book Co., New York, 1928.

⁷ M. LeBlanc and F. Kerschbaum, *Z. physik. Chem.*, **72**, 468 (1910).

amount equivalent to the sodium evolved at the cathode. Mulligan, Ferguson and Rebbeck⁸ found that the anode gas can be obtained directly by electrolysis.

Roberts Austin⁹ found that potassium could not be made to pass through glass, but that lithium could be, and ascribed the difference to the relative atomic volume of the lithium, sodium, and potassium ions. He also found that glass became colored by gold, dissolved either in a mercury or a lead anode. Heydweiller and Kopfermann¹⁰ worked with closed tubes, immersed in a molten salt of the desired metal or a molten mixture containing such a salt to serve as anode and a molten mixture of NaNO_3 and KNO_3 to serve as cathode. Current strengths ranged from 0.0005 to 0.25 ampere. They found that silver and copper gave colored dispersions of metal in glass, which changed color on heating, the silver especially being marked by a change from yellow to intense red above 290° . Barium and strontium caused an increase in the current, and gave bubbly glass which broke on heating. Tin, lead, cobalt, and ferrous iron all caused the glass to become opaque and brittle, and it was assumed that they were present in colloidal condition. Gold, platinum, and uranium apparently did not go into the glass.

An important improvement in the technique of studies on glass conductivity was that of Burt,¹¹ who used the thermionic emission from a heated metallic filament in an ordinary electric-light bulb to complete a direct-current circuit. The bulb was partially immersed in a bath of molten NaNO_3 , and the Na ions discharged by the electrons from the filament condensed on the upper part of the bulb. Faraday's law was found to hold, and as much as 0.3 ampere could be passed through the bulb. Pyrex resistant glass was found not to be suitable for the bulb. With the

⁸ M. J. Mulligan, J. B. Ferguson, and J. W. Rebbeck, *J. Phys. Chem.*, **32**, 779 (1928).

⁹ Roberts Austin, *Proc. Inst. Mech. Eng.*, 1895, Pt. 1-2, 238.

¹⁰ A. Heydweiller and F. Kopfermann, *Ann. Physik*, **32**, 739 (1910).

¹¹ R. C. Burt, *J. Optical Soc. Am. and Rev. Sci. Instruments*, **11**, 87 (1925).

soda glass, potassium ions from a KNO_3 bath did not pass through, but the current quickly dropped to a low value. Lithium ions did penetrate the soda glass, which became white, opaque, and friable and would not hold a vacuum. Zworykin¹² found that potassium from molten KNO_3 did penetrate a soda glass, rendering it brittle, and passed readily through a potassium glass without corroding the glass or rendering it brittle. Hurter¹³ carried on similar experiments. Selenyi¹⁴ confirmed the work of the preceding observers, and also found that when the nitrate bath was made the cathode, the oxygen was electrolytically introduced within the bulb, in amount calculated from the quantity of electricity which had passed.

Hurd, Engel, and Vernon¹⁵ studied the conductivity of glass in a similar manner, using solutions of NaCl , of $\text{Na}_2\text{Cr}_2\text{O}_7$, or of the fused eutectic mixture of $\text{NaNO}_3 + \text{NaNO}_2$, as an electrolytic bath. Metallic sodium was deposited inside the bulb, with no apparent effect on the glass, although at higher temperatures it became brownish. Heating the glass to redness in a flame was without result, and microscopic examination showed no cracking except in the vicinity of bubbles. Potassium ions, from solutions of KCl or from fused KCNS , penetrated easily, but any considerable depth of penetration resulted in fracture of the glass. No potassium could be detected spectroscopically in the sodium collected inside the bulb, but it was detected in a bulb of a special potassium glass. Even in this case, cracking resulted from an hour's electrolysis. Replacement of sodium by lithium ions, from a bath of fused LiNO_3 , proved difficult and the bulbs became opaque and cracked. Transfer of lithium could not be detected with ordinary glass before cracking, but could be detected with a special lithium glass, which, however, cracked after an hour's elec-

¹² V. Zworykin, *Phys. Rev.*, **27**, 813 (1926).

¹³ H. Hurter, *Helv. Chim. Acta*, **9**, 1069 (1926).

¹⁴ P. Selényi, *Ann. Physik*, **84**, 111 (1927); **85**, 643 (1928).

¹⁵ C. P. Hurd, E. W. Engel, and A. A. Vernon, *J. Am. Chem. Soc.*, **49**, 447 (1927).

trolysis. Ammonium ions could be transported through the bulbs, using saturated NH_4Cl solutions or fused NH_4NO_3 , at 110° , without fracturing or discoloring the glass, unless the run was continued for several hours. Heating always caused cracking, and at a dull red countless bubbles appeared along the cracks.

Details of the conduction process have been studied by Ferguson¹⁶ and his co-workers. When a tube filled with mercury is electrolyzed by setting up a potential difference between the mercury and an external conductor such as a liquid electrolyte, gas is evolved at the mercury cathode. The gas was found to be a mixture of oxygen and hydrogen, but not in the proportions to form water. It was concluded that the gas is produced by the action of sodium on sorbed water and the simultaneous electrolysis of the sodium hydroxide produced. No gas was observed with glass in which the sodium had been replaced by silver, and on reversal of the current the gas was largely resorbed. Anode gas could be obtained directly by electrolysis.

Kraus and Darby¹⁷ made a careful study of the conduction process in glass and confirmed many of the previous workers' conclusions. In addition, they made a quantitative study of the replacement of sodium by silver from a fused AgNO_3 bath, in a soda-lime glass containing 16.90% Na_2O , 11.24% CaO (+ PbO), 2.35% $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$. Faraday's law was found to hold accurately, and all the current is carried by the sodium ion. The depth of penetration of silver ion could be measured with a microscope, and hence the speed of the sodium ions calculated from the moving boundary. The results are given in Table 12, speed being measured in centimeters per volt per centi-

¹⁶ J. W. Rebbeck and J. B. Ferguson, *J. Am. Chem. Soc.*, **46**, 1991 (1924); M. J. Mulligan, J. B. Ferguson, and J. W. Rebbeck, *J. Phys. Chem.*, **32**, 779, (1928); *ibid.*, **32**, 843 (1928); M. J. Mulligan and J. B. Ferguson, *Trans. Roy. Soc. Canada (3)*, **21**, 263 (1927).

¹⁷ C. A. Kraus and E. H. Darby, *J. Am. Chem. Soc.*, **44**, 2783 (1922); C. A. Kraus and E. H. Darby, "The Properties of Electrically Conducting Systems," Chemical Catalog Co., New York, 1922, p. 356.

meter. From the composition of the glass the portion of the sodium present which takes part in the electrolysis, i.e., the effective ionization, can be calculated. These results also are included in Table 12. It will be observed that the ionization increases appreciably over the temperature range studied, and it is considered to be probable that ionization is practically complete at temperatures around 1000° C.

TABLE 12

SPEED OF SODIUM IONS, AND EFFECTIVE IONIZATION, IN A SODA-LIME-SILICA GLASS, AT VARIOUS TEMPERATURES

(After Kraus and Darby)

Temperature.....	278° C	295° C	323° C	343° C
Speed.....	4.52×10^{-8}	1.46×10^{-7}	3.26×10^{-7}	5.9×10^{-6}
Per cent ionization.....	76.5	76.8	77.05	82.3

The purely electrolytic character of the conduction process in glass has been questioned by Poole¹⁸ on the basis of some qualitative observations at ordinary temperature. In other experiments Poole¹⁹ found a linear relation between the conductivity and the field strength, represented by the equation $\log K = A + BX$, where K is the conductivity in 10^{-12} reciprocal ohm per centimeter; and X , the potential gradient in megavolts per centimeter. Values of B decreased with the temperature, ranging from 1.50 at 14° to 0.91 at 74°. The influence of dielectric heating was not considered, and it is possible that this may account for the deviation from Ohm's law. Quittner,²⁰ using Schott Geräte glass and Schott 1447 III glass, at field strengths as high as 0.59×10^6 volts per centimeter found the conductivity to be entirely electrolytic.

Practically all investigators agree in ascribing all the conduction to the sodium ion, but it is probable that other conductivity effects are to be considered. There is great need for a more fundamental study of the conduction

¹⁸ H. H. Poole, *Nature*, **107**, 584 (1921).

¹⁹ H. H. Poole, *Phil. Mag.*, **42**, 488 (1921).

²⁰ Franz Quittner, *Sitzber. Akad. Wiss. Wien*, **136**, 151 (1927).

process in glass. At higher temperatures, all the current appears to be carried by the Na ion, but what is the part played by calcium in such a glass? If it is present as calcium ions, why does it not take part in the conduction? What would be the nature of the conductivity in an alkali-free glass, such as wollastonite glass, $\text{CaO}\cdot\text{SiO}_2$? And how would the conductivity in this glass compare with that in a glass of the composition of the $\text{CaO}\cdot\text{SiO}_2$ — SiO_2 eutectic? A thorough study of the conductivity of glass as a function of composition in the ternary system Na_2O — CaO — SiO_2 , and at various temperatures, would be of the greatest value in extending our knowledge not only of the conductivity of glass, but also of the nature of glass itself. The ratio of the conductivity of strained glass to that of annealed glass is as much as three, a difference which is of a different order of magnitude from the effect of strain on other properties. The study of this effect may yield much information as to the constitution of glass.

3. Methods of Measurement of Electrical Conductivity.

—Because of the enormous change in electrical conductivity of glass with temperature, different methods are required in the various temperature zones. Since the conductivity is electrolytic in character, the methods chosen must be such as to eliminate polarization, but this factor is not of importance at ordinary temperatures. Curtis²¹ gives the details of two methods used by him. One of these, illustrated in Fig. 9, is a galvanometer method, using a Sullivan galvanometer with a current sensitivity of 2000 mm per microampere, with a scale distance of 2 meters. The terminal *F* of the battery is connected to the mercury on which the specimen floats. The current flows through the specimen to the mercury contained in an open cylinder of known area which is connected to *D*. The megohm in series serves to protect the galvanometer and is usually negligible relative to the resistance of the specimen. To prevent the current which flows over the surface

²¹ H. L. Curtis, Bull. Bur. Standards, 11, 359 (1914-15).

of the specimen from reaching *D*, a guard ring of mercury surrounds the cylinder, but is insulated from it. This guard ring is connected directly to the opposite terminal of the battery. In measuring any surface resistance in which a guard ring is unnecessary, the unknown resistance is connected directly between *D* and *F*. The key *K*₂ is for short-circuiting the galvanometer; the key *K*₁ closes the circuit through the galvanometer. When the double-

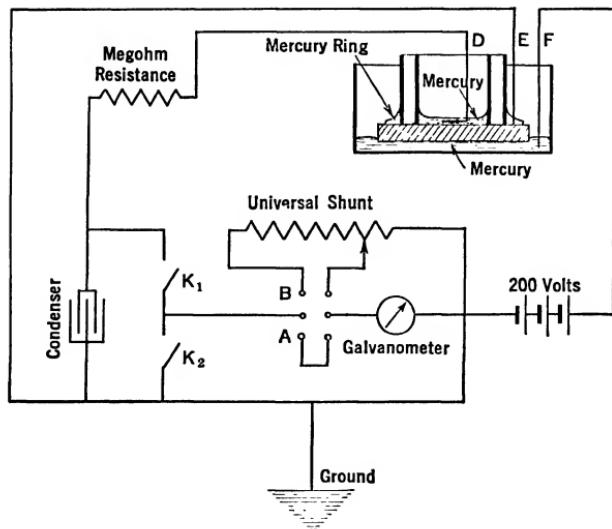


FIG. 9.—Connections for Measuring Volume Resistivity by the Galvanometer Method. After Curtis.

throw switch is in the direction *B*, the galvanometer is connected in parallel with a universal shunt. This can readily be adjusted so that 1, 1/10, 1/100, 1/1000, or 1/10,000 of the total current passes through the galvanometer. Using a battery of 200 volts, resistances from 10^4 to 10^{11} ohms can be measured to an accuracy of 10%. When the double-throw switch is thrown to *A*, the galvanometer is connected directly in series with the specimen without the damping resistance which is contained in the universal shunt. If the current is so small

that it does not produce an appreciable deflection upon closing the key K_1 , the key is opened so that the current flowing through the specimen will charge the condenser. At the end of time t , the key K_1 is again closed and the charge which has accumulated is discharged through the galvanometer. From the ballistic constant of the galvanometer, the resistance of the specimen can be computed in the following manner.

If Q is the quantity of electricity upon the condenser, of capacity C , at the time t , i the current flowing through the specimen, and R its resistance, then

$$E = Ri + Q/C$$

But

$$i = dq/dt$$

hence

$$E = R(dq/dt) + Q/C$$

The familiar solution of this equation is

$$Q = EC (1 - e^{-t/(RC)})$$

From this

$$e^{-t/(RC)} = 1 - [Q/(EC)]$$

and

$$R = -t/(C \log_e [1 - Q/(EC)])$$

Expanding

$$-\log_e [1 - Q/(RC)] = [Q/(EC)] + [Q/(EC)]^2 + \text{etc.}$$

When $Q/(EC)$ is a small fraction, the approximate relation is

$$R = t/[C \cdot Q/(EC)] = Et/Q = Et/(Kd)$$

where K is the ballistic constant of the galvanometer, and d the deflection.

For measuring resistances higher than 10^{15} ohms a Dolezalek quadrant electrometer having a capacity of 130 micro-microfarads was employed. By means of it resistances as high as 10^{17} ohms could be measured. The

diagram of Fig. 10 gives the connections for measuring surface resistivity. The lead to one pair of quadrants is entirely surrounded by an earthed shield; the other pair of quadrants is connected to earth. The surface leakage is over the surface between the inner and outer cyclinders, which rest on the insulator.

To measure the volume resistivity of the specimen the battery B is disconnected from the outer ring and connected

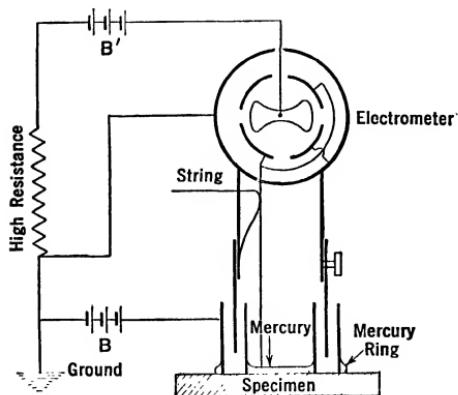


FIG. 10.—Connections for Measuring Surface Resistivity by the Electrometer Method.

After Curtis.

to the mercury on which the specimen is floated. (See Fig. 10.) The outer ring is then connected to earth. The current which flows onto the inner quadrant must now flow through the specimen. If the needle of the electrometer is maintained at a constant potential, the deflection of the needle will depend on the quantity of electricity

on the inner quadrant. If the external electromotive force E is high relative to the counter electromotive force due to the charge on the quadrants, then the current through the insulator may be considered constant. In this case, $R = E/I = Et/Q = Et/(Kd)$, where E is the applied emf, t the time necessary to produce a deflection d , and K the quantity of electricity necessary to produce unit deflection.

In making measurements of high resistivities, due account must be taken of the absorption current, which may not become negligible until some minutes, and may persist for hours. Curtis states that immediately after applying the electromotive force the absorption current may be relatively large, but it decreases rapidly so that at the end of one minute the quantity absorbed per second is

usually between 1/100 and 1/100,000 of the quantity which was displaced through the dielectric. In those cases in

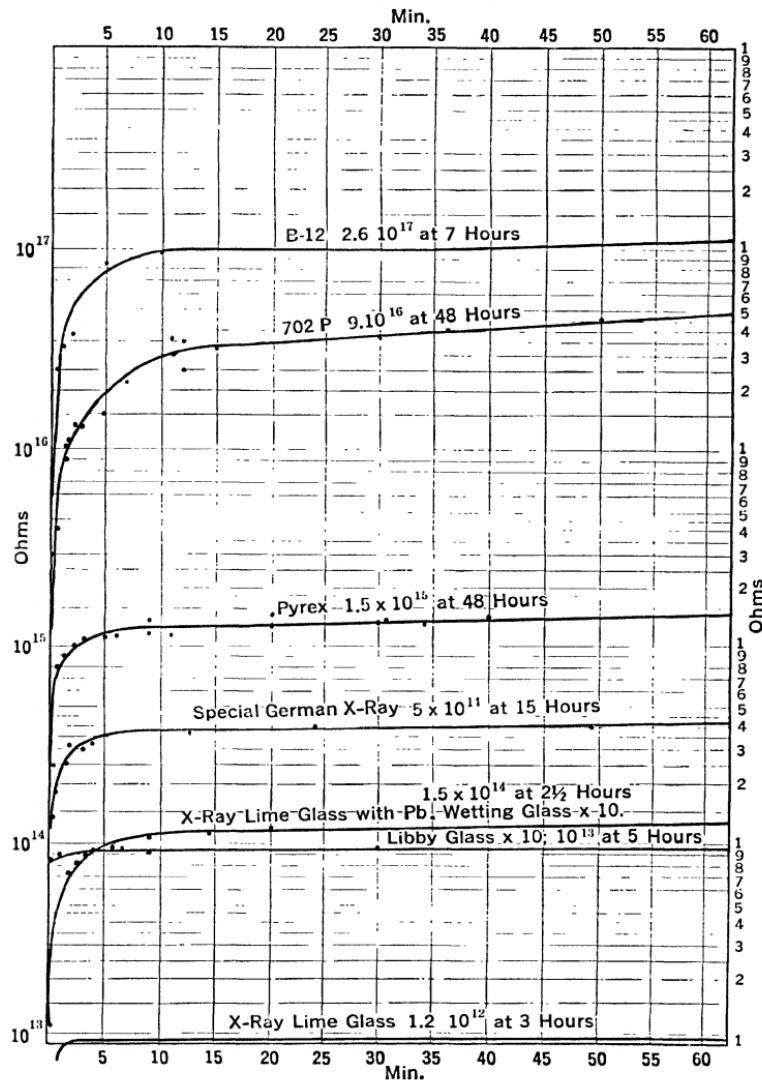


FIG. 11.—Resistance of Dry Glass as a Function of the Time after Applying Voltage. After Bronson.

which the conductivity is less than about 10^{13} ohms, the absorption current gives no error greater than 10%, pro-

vided the resistance is measured at the end of one minute. However, if the resistivity is above 10^{13} ohms, measurements must be made with different time intervals in order to determine when the absorption current becomes negligible. If the resistivity is greater than 10^{16} ohms, the absorption current at the end of one minute will probably equal the conduction current and may be much larger. Bronson,²² studying leakage of insulators for "electrom-

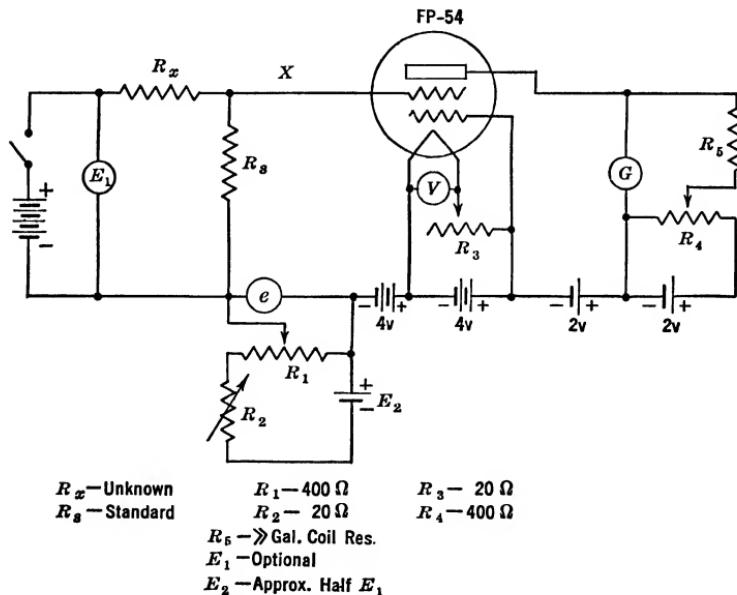


FIG. 12.—Circuit for Measuring High Resistances Using a Pliotron Tube.
After Rose.

eter" tubes, found it necessary to polarize the glass by impressing the operating voltage for some hours before measurements were made. The need for this is shown in Fig. 11, which gives the resistance as a function of the time after voltage is applied. The apparent change in resistance which is due to the absorption current is enormous during the first ten minutes, and is still appreciable after an hour.

In addition to the two standard methods for the

²² H. L. Bronson, cited by A. W. Hull, Physics, 2, 420 (1932).

measurement of very high resistances described above, a third method has recently been developed which makes use of a low grid current Pliotron tube as a current indicator. No results for the resistivity of glass obtained with this apparatus have been published, but Rose ²³ has given a complete description of the circuit, as shown in Fig. 12. When the voltage E_1 is impressed across R_x and R_s in series, it divides in proportion to their resistances:

$$e_x = R_x(R_s + R_x)E_1; \quad e_s = R_s(R_s + R_x)E_1$$

That part e_s of E_1 which appears across the known resistor R_s is impressed on the grid of the FP-54 Pliotron tube in such a direction as to cause an increase in plate current. This increase is indicated by the galvanometer G , the normal plate current having been balanced out by setting R_4 . The voltage e , initially zero, is now increased until the plate current returns to normal, that is, until G again reads zero. At that point

$$e = e_s$$

From this it follows that:

$$R_x = R_s[(E_1/e) - 1]$$

At temperatures above 100° the method used must be such as to prevent polarization of the electrodes. Robinson ²⁴ compared several methods, namely, the use of non-polarizing electrodes, measurement of the instantaneous current, and the use of alternating current of various frequencies. The non-polarizing electrodes were baths of fused sodium nitrite, or sodium thiosulphate, which by supplying the sodium ions prevented the formation of a high-resistance surface layer. The slow rate of current decay made it possible to apply the voltage for a short known interval of time, 1/5 second, and to measure the quantity of electricity passed by the sample with a bal-

²³ G. M. Rose, Jr., Rev. Sci. Instruments, **2**, 810 (1931).

²⁴ D. M. Robinson, Physics, **2**, 52 (1932).

listic galvanometer. The error so introduced was less than 5%. The results with three types of glasses, namely, a soda-lime glass, a lead glass, and Pyrex resistant glass, are shown in Figs. 13, 14, and 15. The samples were in the form of tubes, 20 cm long, sealed at one end, filled with the liquid electrolyte to about 2 cm of the top, and fixed within a larger tube also filled with the liquid electrolyte to the same height. Up to 250° C, mercury was used for both

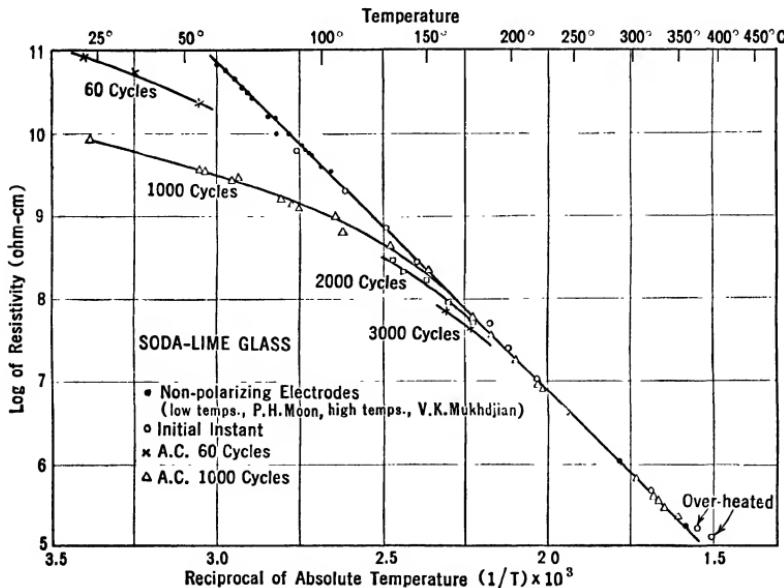


FIG. 13.—The Resistivity of a Soda-Lime Glass as Measured by Various Methods. After Robinson.

electrodes, and above that temperature soft solder. The results with polarizing electrodes agree very closely with those obtained with non-polarizing electrodes over the whole range over which they could be compared, namely, from 60° to 250° C, and the two direct-current methods give a straight-line plot over the whole range from 20° to 520° C. Between 140° and 250° the resistivity as measured with alternating current agrees with direct-current values, but below 140° the alternating-current values become lower,

indicating an additional component of loss. This effect increases remarkably with frequency, both between 60 and 1000 and between 1000 and 3000 cycles. The higher the frequency the higher the temperature at which the additional loss is noticeable. Robinson points out that although this loss can be explained either by the Debye theory of polar

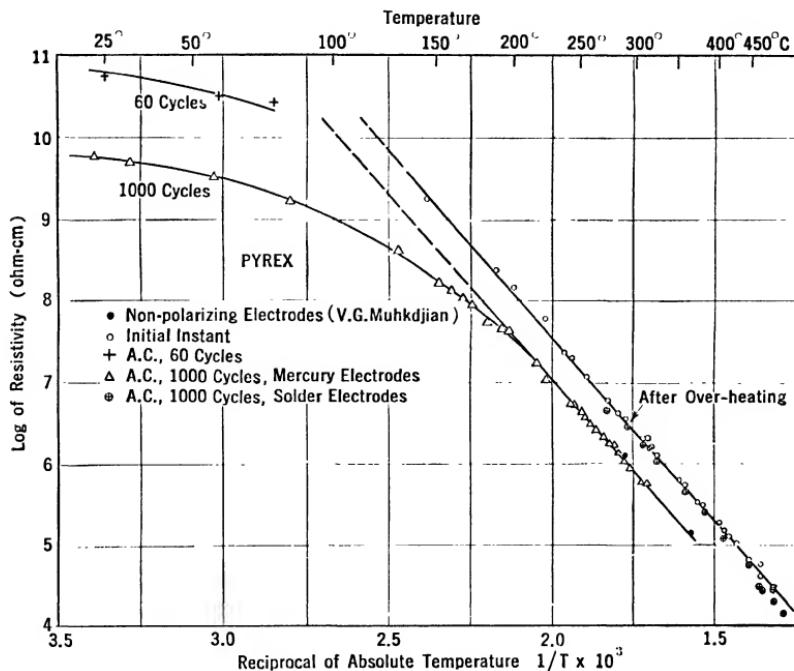


FIG. 14.—The Resistivity of Pyrex Resistant Glass as Measured by Various Methods. After Robinson.

molecules or the Wagner theory of imperfect dielectrics, the lack of evidence as to the existence of polar molecules in glass makes the exact nature of the loss uncertain. No mention is made of the possible effect of dielectric heating in causing this difference, and sufficient data to estimate it are not given, but this effect may account for a major part of the observed difference between direct- and alternating-current methods.

At temperatures near and above the annealing temperature alternating-current methods alone are used. Sutton and Silverman²⁵ used a Vreeeman oscillator, using a frequency of 1000 cycles and platinum electrodes. Fulda²⁶ used a 60 cycle frequency and an electrodynamometer as a current-measuring instrument. Bryson²⁷ introduced an improve-

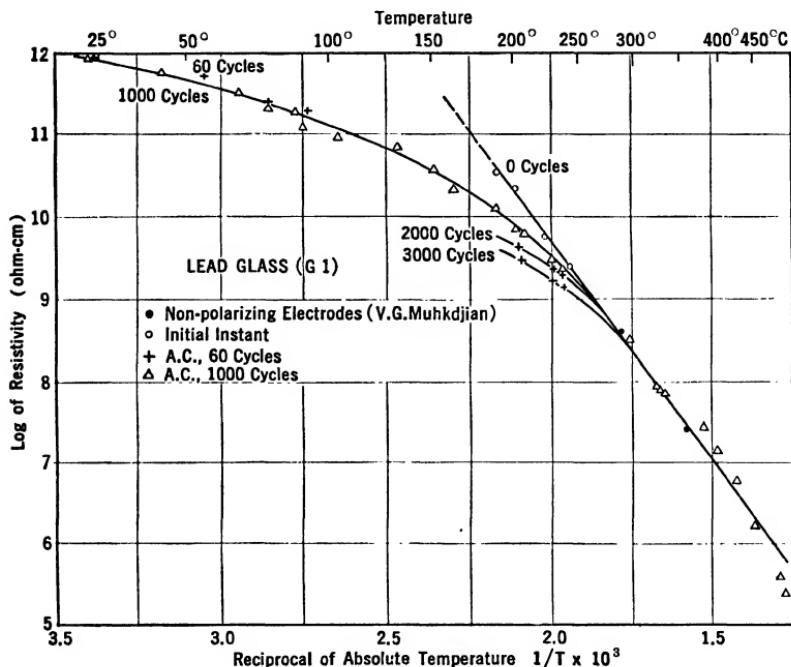


FIG. 15.—The Resistivity of a Lead Glass as Measured by Various Methods.
After Robinson.

ment in technique (shown in Fig. 16), consisting in the use of a vacuum tube as an alternating-current generator. A self-inductance, P , consists of 800 turns of 22 gauge copper wire, wound on an ebonite former, 2.5 in. in diameter, $\frac{3}{4}$ in. thick, with end pieces of $\frac{3}{8}$ -in. ebonite sheet, 5.5 in. in diameter. The self-inductance, S , which is loosely coupled

²⁵ W. J. Sutton and A. Silverman, *J. Am. Ceram. Soc.*, **7**, 86 (1924).

²⁶ M. Fulda, *Sprechsaal*, **60**, 769 (1927).

²⁷ F. F. S. Bryson, *J. Soc. Glass Tech.*, **11**, 331 (1927).

to P , and connected to the grid of the tube, is wound on the top of P and consists of about 1200 turns of 38 gauge copper wire. The tertiary circuit, R , consists of 200 turns of 22 gauge wire wound on a former of 2.5-in. diameter, $\frac{1}{4}$ in. thick. This coil is mounted on a spindle, which also passes through the center of the other coil. Thus the coupling and the reactance can be varied by moving the coils toward or away from each other. The frequency can be varied by altering the capacity, C_1 , in the oscillatory circuit. With a capacity of the order of 0.2 microfarad, a frequency of about 500 cycles per second is obtained, which was used in making the tests.

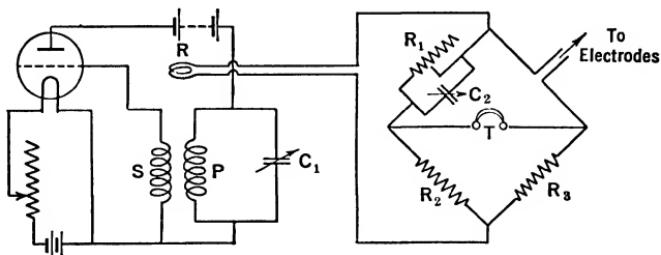


FIG. 16.—A Vacuum-Tube Method for Generating High-Frequency Alternating Current, and a Circuit for Measuring the Resistivity of Glass. After Bryson.

The bridge method used for measuring the resistance of the glass is shown in Fig. 16. R_1 is a three-dial decade resistance having a total resistance of 999 ohms. R_2 and R_3 are ratio arms of 1, 10, 100, and 1000 ohms each. T is a telephone receiver of 120 ohms resistance. C_2 is a battery of condensers with a maximum capacity of about 1.7 microfarads. These condensers are connected in parallel with the variable resistance so as to balance the capacity of the conductivity cell, which varies with the condition of the glass.

The glasses were melted in fire-clay crucibles, 12 mm in diameter, 60 mm deep, which just fitted inside a platinum-wound furnace. Fire-clay tubes with double bore,

having a separation of about 3 mm, were used to hold the electrodes at a definite distance apart and at a definite depth of immersion in the glass. The platinum wires used as electrodes were cemented into this tube, and the exposed portions made exactly 5 mm long and fixed at 3 mm apart. The tube carrying the electrodes was passed through a hole in the crucible, into which it was then cemented. The glass to be tested was first ground to a powder and then dropped, a little at a time, into the crucible and allowed to melt, sufficient glass being added in each case to cover the electrodes to a definite amount. A test made on an empty crucible showed that the resistance of the fire-clay insulation separating the electrodes varied from about 500,000 ohms at 600° to about 50,000 ohms at 1150°. When the cell contained an ordinary soda-lime-silica glass, the resistance was of the order of 350 ohms at the lower temperature and 12 ohms at the higher. The cells were calibrated using solutions of known concentration of NaCl or KCl, the conductivities of which can be obtained from standard tables.

4. Conductivity at Low Temperatures. *Surface Conductivity.*—Since the time of Faraday,²⁸ it has been inferred that part of the conductivity of glass may be ascribed to a film of water condensed on its surface. The existence of such a film was demonstrated by Warburg and Ihmori,²⁹ who showed that near the dew point this film reached a thickness of several millionths of a centimeter, that with the better glasses all the film was removed in a dry atmosphere, and that with inferior glasses all the film could be removed only by heating. The thickness of the adsorbed film on glass has been the subject of many studies, which have been summarized in some of the recent papers.³⁰

²⁸ M. Faraday, Phil. Trans., 1830, part 1, p. 49.

²⁹ E. Warburg and T. Ihmori, Ann. physik. Chem., **27**, 481 (1886).

³⁰ I. R. McHaffie and Sam Lenher, J. Chem. Soc., **127**, 1559 (1925); J. C. W. Frazer, W. A. Patrick, and H. E. Smith, J. Phys. Chem., **31**, 897 (1927); R. Stromberg, Kgl. Svenska Veterskapsakad. Handl., **6' 2'**, 1 (1928).

The problem is a difficult one, and there is no unanimity among the various investigators as to the thickness of the film, or, indeed, if it is merely adsorbed film, or if there is in addition some absorption of water in the glass. It has been held that the film builds up until it becomes a monomolecular layer, at about 50% humidity, which according to the calculations of Yager and Morgan³¹ should be easily detected by its conductivity. It is problematical, however, whether the water arranges itself in an orderly manner over the surface of the glass. It is more probable that certain spots representing a predominately alkaline grouping will collect water in layers many molecules thick, while other spots will have no tendency toward absorption of water. There would then be no continuous layer until the water condensed by the alkaline spots spread out over the water-free areas. Moreover, the layer in question is not one of pure water, but rather is an aqueous alkaline solution of increasing strength, and hence of changing properties. Curtis³² found the surface resistance to vary with the humidity as shown in Fig. 17. The compositions of the glasses were not determined, but the Kavalier glass probably did not differ significantly from No. 2, Table 2. When well cleaned before the experiment, fused silica glass gave a curve which was well above that for the untreated glass, which fell but slowly with increasing humidity and which at 90% still was greater than 10^{13} ohms. Curtis calculated that the conductivity of the film on untreated silica glass, assumed to be 6×10^{-6} mm in thickness, would be accounted for by the presence of 6×10^{-9} gram NaCl. Cleaning reduced the conductivity of the better grades of glass, but did not improve that of the poorer grades.

The most extensive study of the surface conductivity is that of Fulda,³³ who used the series of glasses studied at

³¹ W. A. Yager and S. O. Morgan, *J. Phys. Chem.*, **35**, 2026 (1931).

³² H. L. Curtis, *Bull. Bur. Standards*, **11**, 359 (1914-15).

³³ M. Fulda, *Sprechsaal*, **60**, 769, 789, 810, 831, and 853 (1927).

higher temperatures by Gehlhoff and Thomas (p. 89). The measurements were made in connection with a study of volume conductivity (p. 83). The glasses were heated at 300° to 400°, cooled to 25°, and the conductivity deter-

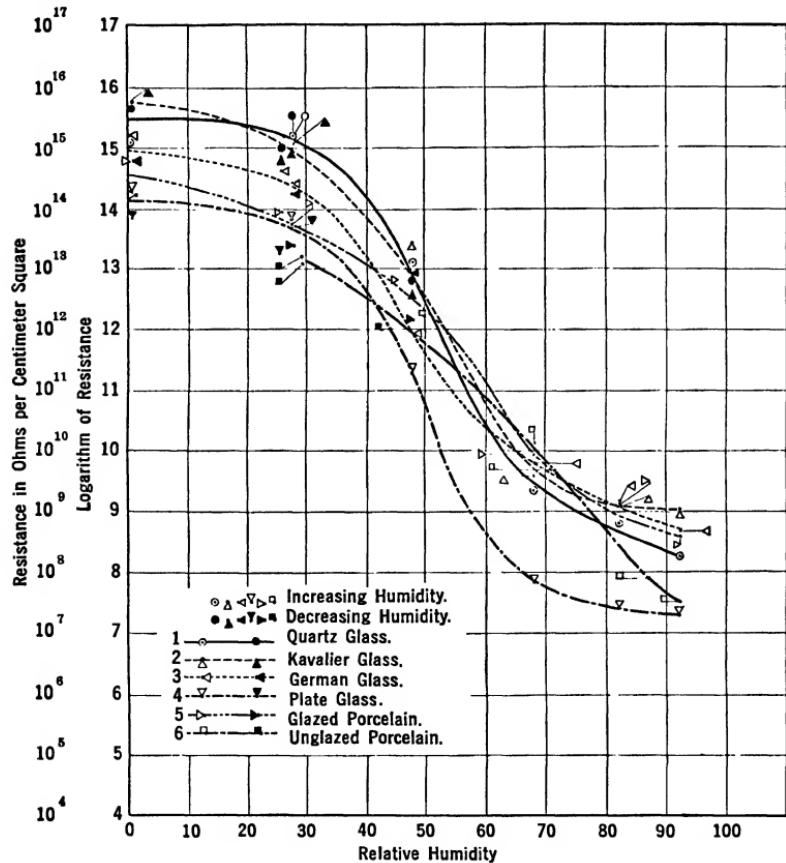


FIG. 17.—The Change of Surface Resistivity with Humidity of Several Substances. After Curtis.

mined. Water-saturated air was drawn over the surface for 15 minutes and the conductivity again determined. The difference between the two conductivity measurements was taken as the conductivity of the surface. The thickness of the surface layer was arbitrarily called unity, and the specific

conductivity of a cylinder of length l and diameter d calculated from the formula: $w_s = wl/d$, in which w_s and w are the specific conductivity and measured conductivity, respectively. The results, expressed as specific resistances, are shown in Fig. 18. The curves "K₂O" and "Na₂O"

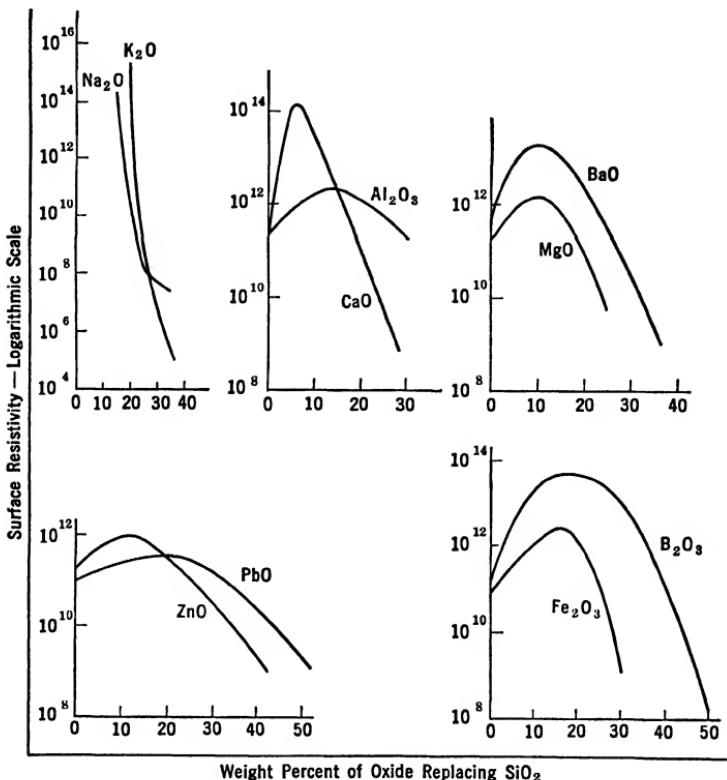


FIG. 18.—The Effect on Surface Resistivity at 25°, 100 Per Cent Humidity, of Replacing SiO₂ in the Glass 0.18 Na₂O, 0.82 SiO₂ by the Indicated Percentage by Weight of Other Oxides. After Fulda.

refer to replacement of SiO₂ by K₂O or Na₂O, in a glass of the initial composition 0.20 PbO, 0.80 SiO₂. An increase in the alkali content results in an immediate and rapid decrease in the surface resistivity. Up to 30% K₂O the potash glasses are the more resistant, but on further increase in the alkali content the soda glasses diminish in resistivity

less rapidly than before, and become superior to the potash glasses. All the other curves refer to the progressive substitution for SiO_2 of the indicated oxide in a glass of the initial composition 0.18 Na_2O , 0.82 SiO_2 . Each of these replacements has an initial beneficial effect on the surface resistivity, which passes through a maximum, after which further substitution has a deleterious effect. The maxima are found at 6% CaO and Al_2O_3 , 10% CaO and MgO , 12% ZnO , 16% Fe_2O_3 , 20% B_2O_3 , and 21% PbO . The figures refer only to replacements in the particular glass studied by Fulda, and do not necessarily have any bearing on similar replacements in a glass of any other initial composition in the binary system Na_2O — SiO_2 , or still less in more complex glasses. Other studies, considered below, indicate that the time of 15 minutes allowed by Fulda for attainment of equilibrium was quite inadequate, and the figures are to be regarded as a measure of the speed of surface attack rather than as equilibrium values.

Yager and Morgan³⁴ made a special study of the surface conductivity of Pyrex resistant laboratory glass as determined by both the humidity and the frequency. Their results are represented by Fig. 19, in which the surface conductivity is plotted against per cent of relative humidity at 25° and at 50° and for frequencies ranging from 1 to 100 kc. They found that with low humidities 2 hours was usually sufficient to obtain constant values, but at higher humidities much longer times were necessary. At 30 kc and 25°, equilibrium was not attained in 20 hours, and at 50° and 95% humidity it was impossible even to approach equilibrium. It should be emphasized that the results of Fulda are not comparable with those of Yager and Morgan, because of the failure of Fulda to secure equilibrium. Great care must be taken in comparing the surface properties as measured by different investigators to insure that the experimental conditions are comparable, a matter particularly important when the property in question is deter-

³⁴ W. A. Yager and S. O. Morgan, *J. Phys. Chem.*, **35**, 2040 (1931).

mined by the rate of a chemical reaction, as is the case with surface conductivity.

Bronson,³⁵ working in the research laboratories of the General Electric Co., studied insulation leakage and found

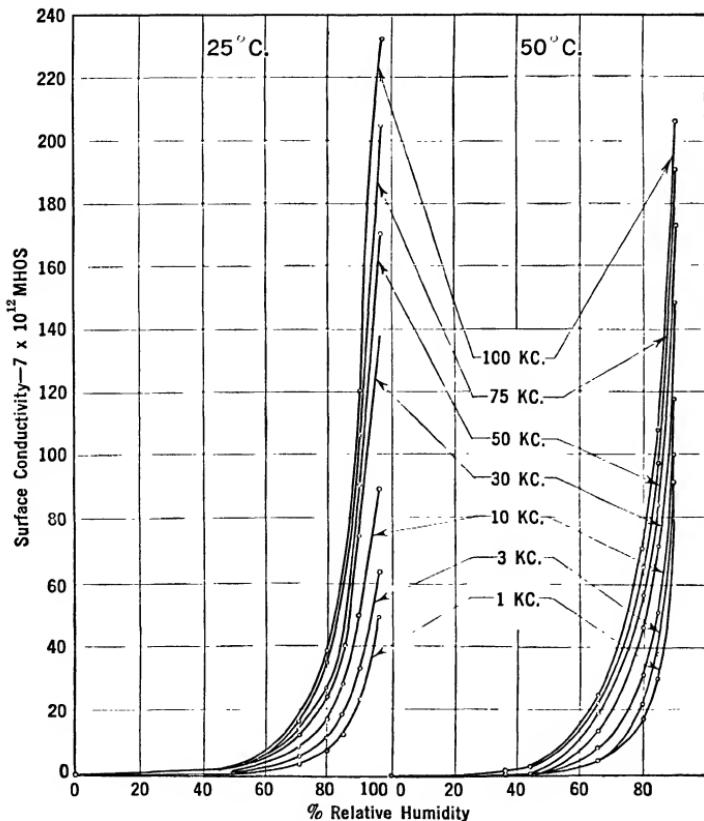


FIG. 19.—The Surface Conductivity of Pyrex Resistant Glass at 25° C and at 50° C for Various Frequencies as a Function of Relative Humidity. After Yager and Morgan.

that the better commercial glasses are satisfactory insulators for the most sensitive "electrometer" tubes, provided the glass is clean and properly "polarized." Cleanliness is paramount. "Quartz insulators" (probably silica glass), mounted in vacuum, leak badly if they have been touched

³⁵ H. L. Bronson, cited by A. W. Hull, Physics, 2, 420 (1932).

with the fingers before mounting. Fig. 20 gives the variation of resistance with temperature above ambient of some typical glasses, and "quartz" on a humid summer day. This shows that clean glass can be used without serious

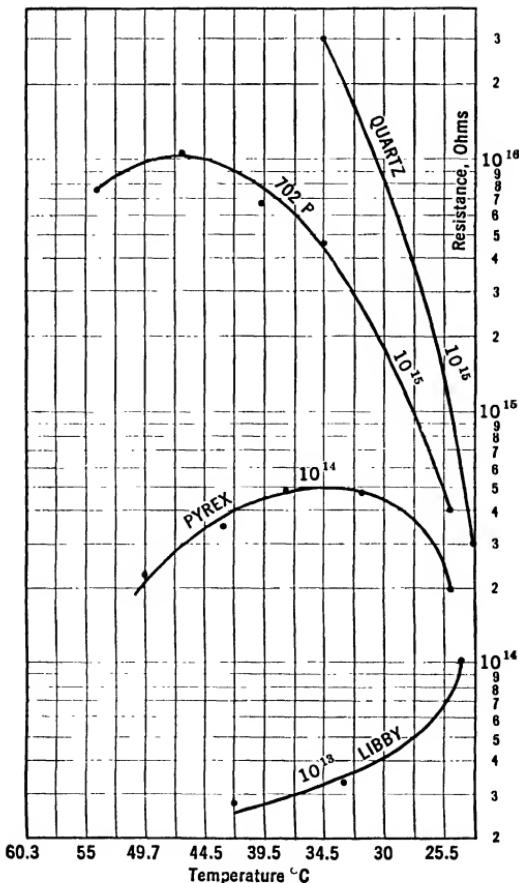


FIG. 20.—The Variation of Resistance with the Temperature above Ambient, on a Humid Summer Day. After Bronson.

leakage if the temperature is raised a few degrees above that of the surrounding air. The sample marked "Libbey" is a high-melting steam-gauge tubing; the immediate increase in conductivity indicates that the volume conductivity predominates over surface leakage. Corning 702P

and Pyrex resistant glass showed optimum temperatures above ambient of 20° and 10° respectively for the particular form tested. The total resistivity of silica glass with its negligible volume leakage increases with increase in temperature. The results of such experiments, however, depend on the absolute magnitude of humidity, on ambient temperature, and on insulator shape.

Studies of surface conductivity agree in showing that in inferior glasses it may greatly exceed the volume conductivity, but that with the better grades of glasses, properly handled, it is entirely negligible. Proper handling includes absolute cleanliness, maintenance of a humidity well below saturation (better well below 50%), and proper polarization. The measure of moisture content in the atmosphere is usually given as a percentage humidity, but it may be that the absolute moisture content would be a better measure. Carried out under proper conditions, the measurement of surface conductivity might be an excellent method of comparing the relative resistance of glasses to weathering.

Volume Conductivity.—One of the first to demonstrate that glass itself has a real electrical conductivity was Ekman,³⁶ who studied the rate of dissipation of an electrical charge from a Leyden jar. Five glasses were compared as to their electrical and chemical stability, and it was found that, although two glasses inferior in chemical stability were also poor insulators, in another comparison the glass which showed inferior chemical stability was a superior insulator. He concluded that most of the charge was dissipated by conduction through the glass, and that Na₂O gives a conducting, K₂O a non-conducting, glass.

T. Gray³⁷ and A. Gray and Dobbie³⁸ measured the variation of resistance with temperature up to 140° of a number of glasses, summarized in Table 13. They con-

³⁶ F. L. Ekman, *Phil. Mag.*, **4**, 39 (1870)

³⁷ Thomas Gray, *Proc. Roy. Soc.* **34**, 199-208 (1882). T. Gray, A. Gray and J. J. Dobbie, *Proc. Roy. Soc.*, **36**, 488 (1884).

³⁸ Andrew Gray and J. J. Dobbie, *Proc. Roy. Soc.*, **63**, 38 (1898); **67**, 197-207 (1900).

TABLE 13
THE SPECIFIC RESISTANCE AND DIELECTRIC CONSTANT OF GLASSES OF KNOWN COMPOSITION
(After Gray and Dobbie)

Number	Density	Temperature, Degrees C	Specific Resistance, Ohms $\times 10^{10}$	K	Composition						
					SiO ₂	B ₂ O ₃	Na ₂ O	K ₂ O	MgO	BaO	$\frac{\text{Al}_2\text{O}_3}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}$
21	3.495	15	7,966	50.5	7.966	7.630	Tr	6.93	42.14
22	3.591	130	18,000	44.5	7.991	7.991	0.5	8.0	46.6
		14	35,000								MnO
23	3.565	135	59,000	8.5	33.0	12.0	Tr	Tr	48.0	1.0	6.0
24	3.493	15	596.5	7.54	67.6	8.0	10.0	Tr
25	2.487	43	0.2	531.1	6.26	69.04	5.0	ZnO	0.4	1.31
		140	0.2	69.2					9.0		2.73
		11	55	11.9					CaO		
		72	72	1.9					7.59		
		93	93	11.9							
		116	116	1.9							
		129	129	0.2							
		149	149	0.2							
26	2.99	10	18,034	7.06	58.83	7.35	6.42	MnO	0.81
		66	66	1,956.5							
		88	88						PbO	26.10	0.43

cluded that a substitution of potassium or barium for sodium in a glass of complex composition increases the resistivity, and also that a glass approaching a definite compound in composition has a high resistance. This last conclusion is fallacious: the evidence, for example, is that glass (21), which is capable of being expressed by a "simple" chemical formula, $2\text{K}_2\text{O} \cdot 5\text{PbO} \cdot 22\text{SiO}_2$, has a high resistivity, but no evidence is presented that such a compound exists. The mere chance that a glass composition can be approximately represented by a more or less complex formula has no bearing on the existence of a compound represented by that formula.

Curtis³⁹ found the volume resistivity of fused silica, in ohm-centimeters, at 22° C, to be over 5000×10^{15} ; of Kavalier glass (probably near to No. 2, Table 2), 8×10^{15} ; of plate glass, 20×10^{12} ; of opal glass, 1×10^{12} . He also found a slight change in resistivity with applied emf, $R_{50V}/R_{500V} = 0.7$, and the ratio of resistivities at 30° and 20° to range from 2.5 to 4.5.

McDowell and Begeman⁴⁰ measured the apparent resistivity at 20° of six glasses: two lead glasses of unknown composition, Nos. 1 and 3; three borosilicates not containing any heavy metals, Nos. 2, 4, and 5, of which No. 2 was Pyrex chemical resistant glass; and No. 6, a lead borosilicate. The resistivity was measured after a brief unmeasured interval of time after the application of the potential difference, and therefore the results obtained are undoubtedly lower than the final resistivity. Following are the values found for specific resistivity at 20°:

Glass No.	Specific Resistivity
1	2.3×10^{13}
2	3.1×10^{14}
3	2.0×10^{15}
4	2.5×10^{15}
5	3.5×10^{16}
6	8.1×10^{19}

³⁹ H. L. Curtis, Bull. Bur. Standards, **11**, 359 (1914-15).

⁴⁰ L. S. McDowell and H. Begeman, Phys. Rev., **31**, 476 (1928).

The extensive measurements of Fulda⁴¹ have greatly increased our knowledge of the resistivity of glass as a function of composition. The glasses were heated at 300° to 400° C, cooled to 25° in a dry atmosphere, and

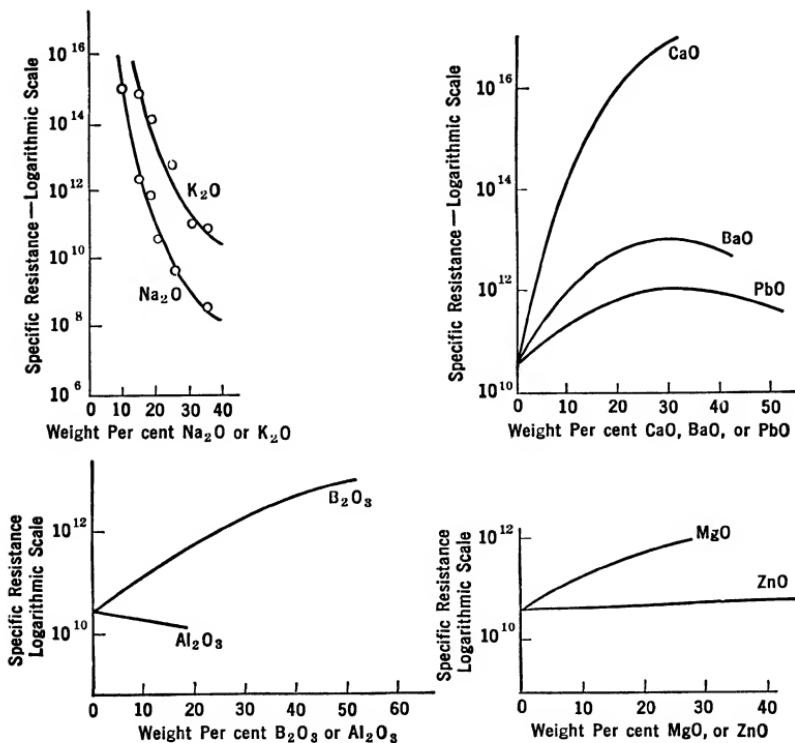


FIG. 21.—The Effect on Specific Resistance of a Glass, 0.18 Na₂O, 0.82 SiO₂, of Replacing SiO₂ by the Indicated Percentage by Weight of Other Oxides. After Fulda.

measured. His scheme of variation of glass composition is explained on p. 73; the results are assembled in Fig. 21.

Replacing SiO₂ by Na₂O or K₂O in a glass containing 20% PbO, 80% SiO₂ results in a rapid decrease in resistivity, the potash glasses being the poorer conductors. Replacement of SiO₂ by Al₂O₃ also lowers the resistivity,

⁴¹ M. Fulda, Sprechsaal, 60, 769, 789, 810, 831, 853 (1927).

although in a much less degree. All other replacements increase the resistivity, the effect being greatest with CaO and least with ZnO. The curves for BaO and PbO pass through well-marked maxima, and it is probable that some of the other curves would show a similar behavior if sufficiently prolonged. It must be remembered that these curves represent but an arbitrary excursion into the three-component system along one straight line, and it is not to be inferred that a curve of similar shape would result from an excursion along another straight line, or with an initial glass of any other composition. The inclusion of an addi-

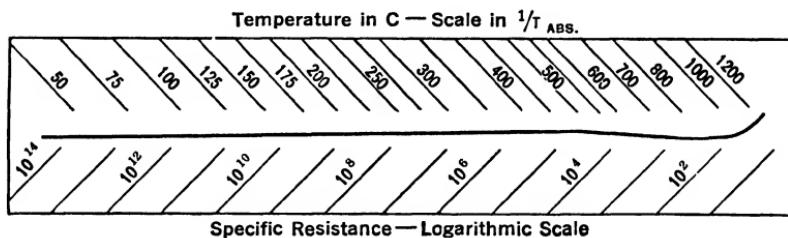


FIG. 22.—The Change in Specific Resistance of a Glass with Temperature.
After Fulda.

tional component will affect the curve in an unpredictable manner.

5. The Effect of Temperature on Electrical Conductivity.—The electrical conductivity of glass increases rapidly with temperature, the specific resistivity of some glasses decreasing from 10^{12} to 10^{15} or higher to around 10^4 ohms at the annealing temperature, reaching unity at 1200° to 1500° . The variation of specific resistivity with temperature is well shown by the curve of Fig. 22, reproduced from Fulda,⁴² in which the logarithm of the specific resistivity is plotted against $1/T$, the reciprocal of the absolute temperature. From 25° to 460° the curve is a straight line, represented by the formula:

$$\log W = (A/T) + B$$

⁴² M. Fulda, Sprechsaal, **60**, 769, 789, 810, 831, 853 (1927).

deduced by Rasch and Hinrichsen⁴³ on a questionable basis from Van't Hoff's equation. At 460° the plotted curve shows a break; from 460° to 650° the results are fitted by a second straight line; and above 650° the temperature coefficient decreases markedly. The Thuringian glass used had the composition: SiO₂ 71%, Na₂O 12.5%, K₂O 8.7%, CaO 5.4%, Al₂O₃ 2.4%; and the constants *A* and *B*, respectively, for the middle range were 6.021 and 3.484. This is the only case in which the resistance of a glass has been determined from room temperature to 1200°.

The break in the straight-line relationship between resistivity and the reciprocal of the absolute temperature, which is usually found near the temperature at which the glass is annealed, has been assumed to be of theoretical significance. The temperature so determined has been called the "Transformation temperature," and has been proposed as a significant item in glass specifications. However, Littleton⁴⁴ has shown that this apparent discontinuity is due, not to a transformation, but to a delayed change in the properties of the glass. In the usual method, the glass is heated at the rate of 5° per minute. If the rate is diminished the temperature of the break is altered; and if the glass is maintained at each temperature until the conductivity has reached a constant value, the curve becomes a smooth one, without a break. Over a small temperature range the resistivity may be represented as a linear reciprocal function of the temperature; but over a large temperature range a real curvature becomes manifest. The viscosity apparently follows a similar law, although it changes much more rapidly with temperature than does the viscosity. Littleton compared the variation with temperature of viscosity and resistivity, and his results are reproduced in Figs. 23, 24, 25, and 26. With a lead borosilicate glass, shown in Fig. 23, the viscosity varies with the

⁴³ E. Rasch and F. W. Hinrichsen, *Z. Electrochem.*, **14**, 41 (1908).

⁴⁴ J. T. Littleton, *Ind. Eng. Chem.*, **25**, 748 (1933).

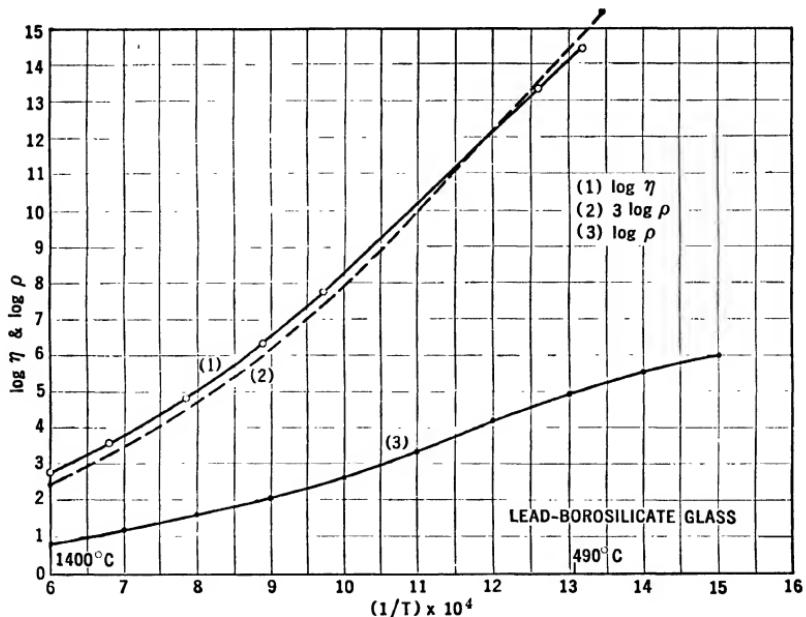


FIG. 23.—Comparison of the Change with Temperature of the Resistivity and the Viscosity of a Lead-Borosilicate Glass.

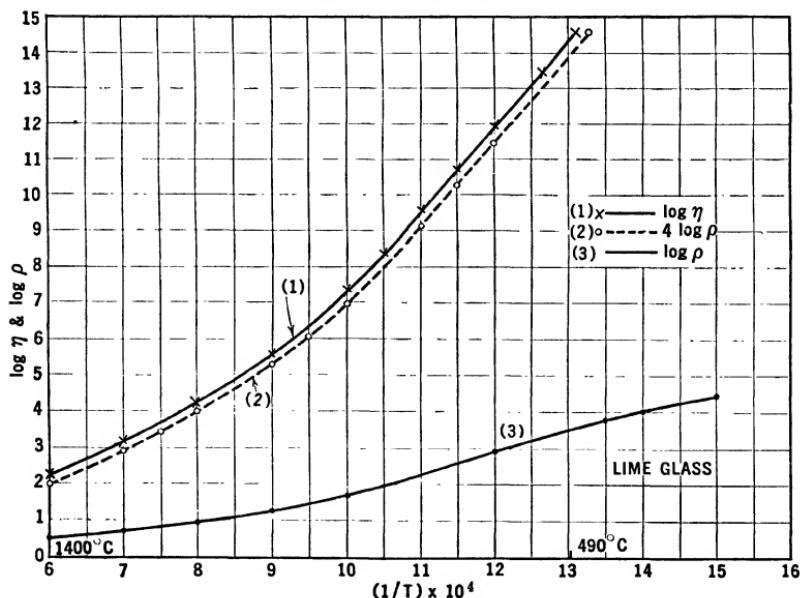


FIG. 24.—Comparison of the Change with Temperature of the Resistivity and the Viscosity of a Lime Glass.

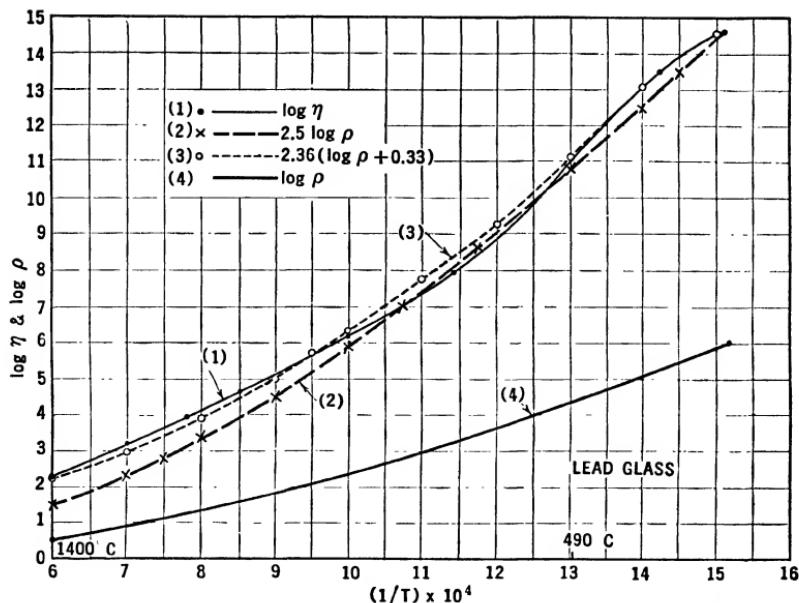


FIG. 25.—Comparison of the Change with Temperature of the Resistivity and the Viscosity of a Lead Glass.

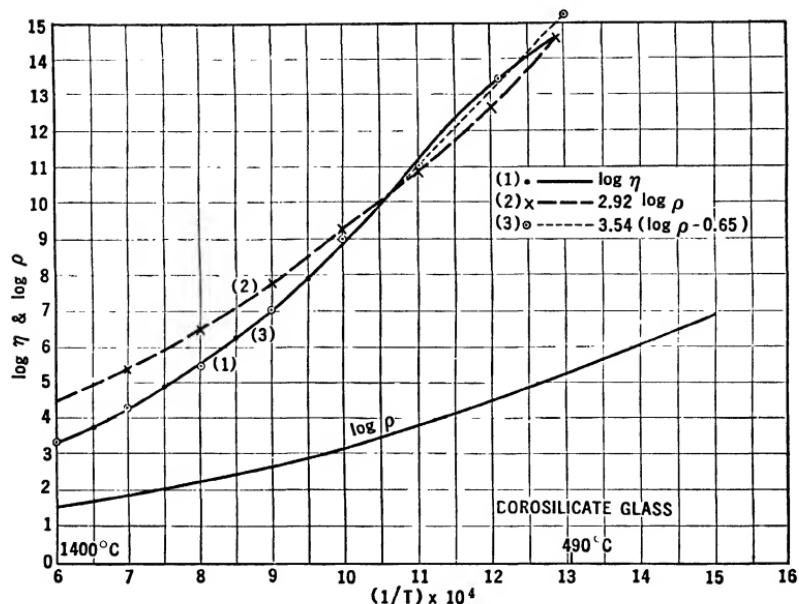


FIG. 26.—Comparison of the Change with Temperature of the Resistivity and the Viscosity of a Borosilicate Glass.

cube of the resistivity; with a lime glass, Fig. 24, it varies as the fourth power of the resistivity; with a lead glass, Fig. 25, and with a borosilicate glass, Fig. 26, the relationship is of the form

$$\log \eta = a \log w - b$$

or

$$w = b' \eta^{1/a}$$

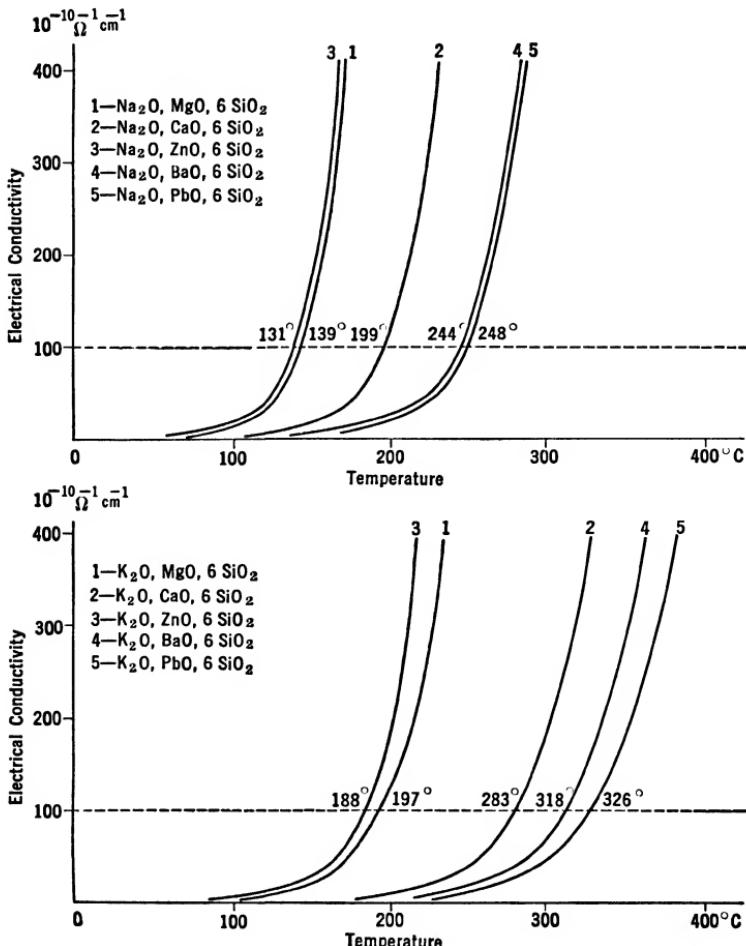


FIG. 27.—The Change of Electrical Conductivity with Temperature of a Series of Glasses Having the General Composition Na_2O (or K_2O), MeO , 6SiO_2 . After Gehlhoff and Thomas.

Littleton remarks, "If the dissociation of the alkali ions does not vary greatly with temperature, then it is strange that resistance is not proportional to viscosity in a more intelligible fashion. Possibly this means that molecular viscosity and finite volume viscosity are two very different

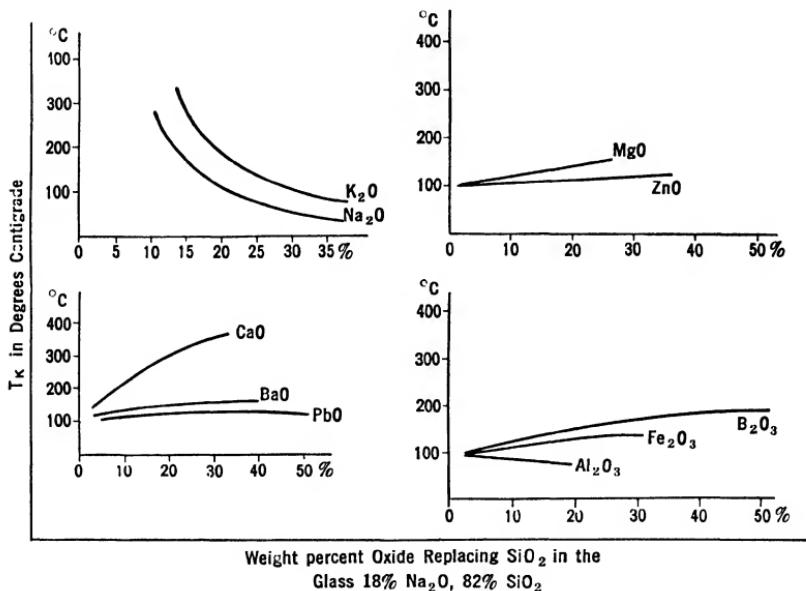


FIG. 28.—The Temperature at which the Specific Conductivity Becomes 100×10^{-10} Plotted Against the Percentage by Weight of the Indicated Oxide Replacing SiO_2 in the Glass, 0.18 Na_2O , 0.82 SiO_2 . After Gehlhoff and Thomas.

quantities, not being by any means proportional to one another."

Gehlhoff and Thomas⁴⁵ made measurements in the temperature interval from 100° to 400° on glasses of systematically varied composition, some of which were further studied by Fulda.⁴⁶ Fig. 27 shows the variation in conductivity with temperature of a number of glasses of the general composition Na_2O (or K_2O)· $M\text{eO}$ · 6SiO_2 , in

⁴⁵ G. Gehlhoff and M. Thomas, *Z. tech. Physik*, **6**, 544-54 (1925).

⁴⁶ Op. cit.

which *MeO* represents MgO , CaO , ZnO , BaO , and PbO . The relation between temperature and resistivity followed the relation of Rasch and Hinrichsen.

In order to compare the effect of variation in composition on the conducting power of glass, the temperature at which the specific conductivity became 100×10^{-10} ohm $^{-1}$ cm $^{-1}$ was chosen for comparison. Fig. 28 refers to this arbitrary standard.

Fig. 28 shows that the alkalies greatly increase conductivity, Na_2O more so than K_2O . Al_2O_3 also increases the conductivity, though but slightly; ZnO , MgO , PbO , Fe_2O_3 , BaO , B_2O_3 , and CaO decrease the conductivity, although all except CaO have but little effect. Studies of several series of four-component glasses containing both Na_2O and K_2O showed that the presence of both alkalies gave a poorer conducting glass than either alone, the minimum conductivity being at a $\text{Na}_2\text{O} : \text{K}_2\text{O}$ ratio of about 1 : 4. Gelhoff and Thomas summarize their results in Table 14, in which the average values of $T_x = 100$ for an addition of 1% of the given oxide are given, for each 5% composition range.

TABLE 14

THE CHANGE IN $T_x = 100$, PER 1% OF ADDED OXIDE, ON REPLACING SiO_2 BY THE INDICATED OXIDE, AS AFFECTED BY ITS PERCENTAGE IN THE GLASS

(After Gehlhoff and Thomas)

Percentage Content of the Added Oxide

	0-5	5-10	10-15	15 20	20 25	25-30	30-35	35-40	40 50	50-60
B_2O_3 ...	+ 3.0	+ 3.0	+ 2.8	+ 2.1		+1.3		+1.0		+0.9
Na_2O	- 27	- 9.4	- 6.6	- 5.4	- 2.4			
K_2O	- 36	- 16.2	- 8.6	- 6.6	- 5.6			
CaO ...	+14	+10	+ 8	+ 7.0	+ 6.6	+ 6.2				
BaO ...	+ 2.5	+ 2.3	+ 2.0	+ 1.7	+ 1.4	+ 1.0	+ 0.6	+0.3		
ZnO ...	+ 0.6	+ 0.5	+ 0.5	+ 0.5	+ 0.5	+ 0.5	+ 0.5			
PbO ...	+ 1.4	+ 1.3	+ 1.0	+ 0.7	+ 0.6	+ 0.4	+ 0.3	+0.0	-0.5(μ)	
MgO ...	+ 1.2	+ 1.4	+ 1.4	+ 2.3	+ 2.9					
Al_2O_3 ...	- 0.9	- 0.9	- 0.9							
Fe_2O_3 ...	+ 2.0	+ 2.0	+ 1.8	+ 1.3	+ 0.7					

Sutton and Silverman⁴⁷ measured the conductivity of a glass of the composition SiO_2 67.37%, Na_2O 15.60%, CaO 16.74%, Al_2O_3 0.41%, Fe_2O_3 0.09%, from 750 to 1100°, as a part of their study of the effects of NaCl on the conductivity of glass. Their results are shown in Fig. 29.

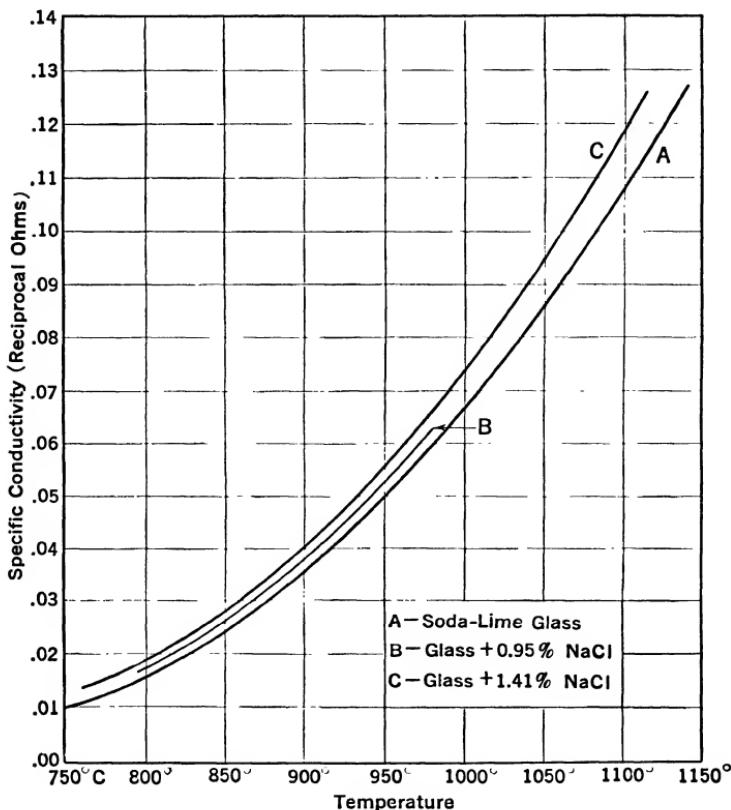


FIG. 29.—The Change of Specific Conductivity with Temperature of a Soda-Lime Glass and the Effect of Addition of NaCl . After Sutton and Silverman.

Bryson⁴⁸ measured the conductivities of a number of experimental glasses from below 600° to 1150° using a frequency of 500 cycles. The compositions of his glasses

⁴⁷ M. Sutton and A. Silverman, *J. Am. Ceram. Soc.*, **7**, 86 (1924).

⁴⁸ F. F. S. Bryson, *J. Soc. Glass Tech.*, **11**, 331 (1927).

are given in Table 15; the conductivity results in Fig. 30. Detailed results are not given.

TABLE 15
COMPOSITIONS OF GLASSES USED BY BRYSON

Glass No.	SiO ₂	Na ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃
G 1 B.....	77.57	21.89	0.38	0.17
G 1 C.....	72.95	26.21	0.63	0.17
G 1 D.....	65.69	31.64	0.58	1.45	0.25
G 1 F.....	58.89	38.33	0.50	2.09	0.24
G 2 A.....	80.05	16.23	2.70	0.57	0.09
G 2 C.....	75.95	15.38	0.50	6.49	1.27	0.08
G 2 D.....	74.60	15.25	8.76	0.83	0.07
G 5 A.....	75.70	21.21	0.20	2.29	0.11
G 5 C.....	73.45	17.81	0.20	8.47	0.13
G 5 E.....	72.00	14.07	13.01	0.14

The work of Gehlhoff and Thomas, Fulda and Bryson constitutes a beginning of the study of the electrical conductivity of glass as a function of the composition, but nothing more. As was emphasized in the discussion of density, it is not possible to deduce the effect of the various components of even a three-component system on the basis of a single short excursion into the ternary field, and so far there has been but little even of that. The relationships become even more complicated with commercial glasses, which always contain several components concerning whose specific effect valid conclusions cannot be drawn. There is great need of further study, to ascertain the specific effects of the various components, the part played by each in the process of conduction, and the effect of temperature on the conduction process.

Numerous other measurements have been made on the conductivity of glasses of various compositions and at various temperatures by Foussereau,⁴⁹ Thomson,⁵⁰ Am-

⁴⁹ G. Foussereau, *J. phys.*, **11**, 254 (1883).

⁵⁰ W. Thomson, *Proc. Roy. Soc.*, **23**, 468 (1875).

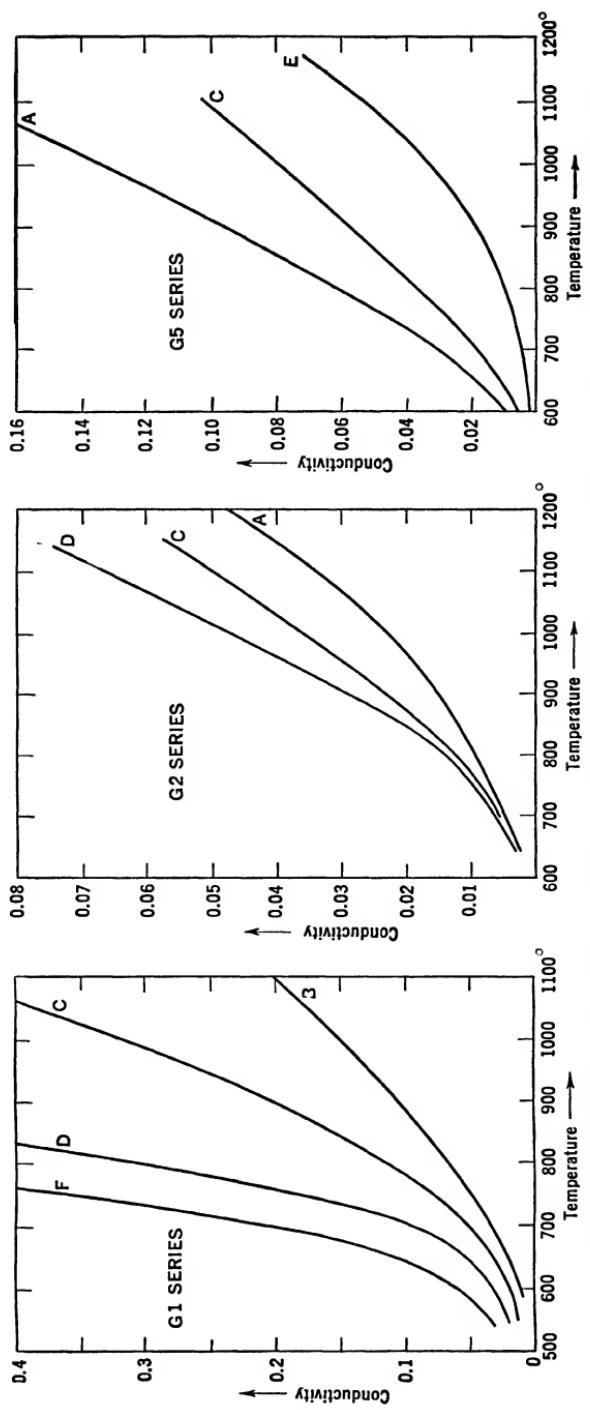


FIG. 30.—The Change of Conductivity with Temperature of the Glasses Whose Compositions Are Given in Table 14. After Bryson.

bronn,⁵¹ Baumeister,⁵² Doelter⁵³ and Bolle.⁵⁴ Some of the measurements on known glass types are assembled in Table 16; the first group is by Bolle; the second by Baumeister. Bolle also measured three glasses whose compositions were near: SiO_2 69%, Na_2O 17%, ZnO 5%,

TABLE 16
ELECTRICAL RESISTIVITY AND CONDUCTIVITY

(a) Resistivity

Pyrex Resistance Glass (No. 1, Table 2) Surface Resistivity;* 10^{14} ohms at 34% humidity; 5×10^8 ohms at 84% humidity. Volume resistivity,* 10^{14} ohm-cm.

(b) Conductivity, K

No. in Table 2	Unit 10^{12} ohm $^{-1}$ cm $^{-1}$ †				
	100°	125°	150°	175°	200°
8	0.012	0.0703	0.334	1.59	6.90
33	0.0132	0.0672	0.425	2.32	
37 ca.	0.00542	0.0418	0.221	1.57	7.69
42 ca.	0.0190	0.0416	0.0968	0.5076	2.38
48 ca.	0.0025	0.015	0.0684	0.668	2.544
63	0.00256	0.0134	0.0406	0.106	0.374
61 ca.	0.00233	0.00994	0.039	0.116	0.393

	Unit: 10^8 ohm $^{-1}$ cm $^{-1}$ ‡							
	t°	K	t°	K	t°	K	t°	K
7	250	12.9	402	400.8	502	1300	602	5000
32	250	0.677	400	41.58	489	210		
30	250	0.25	409	9.08	500	34.5	600	1178

* Corning Glass Works, Corning, N. Y. † Bolle, Dissertation, Berlin (1900).

‡ Baumeister, Dissertation, Rostock (1912).

⁵¹ R. Ambronn, Diss., Berlin, 1900, F. Eckert, Jahrb. radioakt. Elektronik, **20**, 93 (1923), p. 190.

⁵² F. Baumeister, Physik. Z., **14**, 112 (1913); Ann. Physik, **58**, 139 (1919).

⁵³ C. Doelter, Handbuch der Mineralchemie, vol. 1, p. 712, Steinkopf, Dresden (1912).

⁵⁴ E. Bolle, Diss., Rostock (1912); Fortschr. Physik., **1**, 399 (1912).

PbO 8%, Al₂O₃ 1%, and found the following conductivities in mhos $\times 10^{10}$: at 100°, 1.0; 150°, 17; 200°, 178.

Two of the obstacles to all physical measurements on glass are the difficulty of getting it into a reproducible state and the uncertainty as to what is to be taken as the standard state. The effect of annealing in all its aspects is an example—annealing not merely to remove mechanical strain, but also to define the state of the glass. This is a factor which has been insufficiently considered in the work which has appeared hitherto. It is known from the results of Foussereau,⁵⁵ of Fulda,⁵⁶ and of Mulligan, Ferguson, and Rebbeck⁵⁷ that annealing decreases the conductivity of glass; but no adequate study which separated the various factors involved has yet appeared. It is usually found that the ratio of resistivities of strained and annealed glass is at least 1 : 3. No adequate theoretical explanation has been advanced, and it is probable that none will be forthcoming until much more is known not only about the conduction process in glass, but also about the constitution of glass. Studies of the conduction process offer a promising method for the study of the constitution of glass.

Another factor to be considered in precise measurements is the content of volatile components in the glass. Of these, water predominates, and that it, as well as the other volatile substances present, will exert a profound effect is highly probable. Bush and Connell⁵⁸ found that the volume resistivity was increased in a ratio of 6 : 1 by heating glass in *vacuo* to 350°; on exposure to air the resistivity again decreased. This opens an interesting field for future study and emphasizes the importance of precise definition of the composition of the glass studied, not only in regard to major constituents, but also in regard to accessory ingredients.

⁵⁵ G. Foussereau, *Compt. rend.*, **96**, 785 (1883).

⁵⁶ M. Fulda, *Sprechsaal*, **60**, 769, 789, 810, 831, 853 (1927).

⁵⁷ M. J. Mulligan, J. B. Ferguson, and J. W. Rebbeck, *J. Phys. Chem.*, **32**, 779 (1928).

⁵⁸ V. Bush and L. H. Connell, *J. Franklin Inst.*, **194**, 231–40 (1922).

Sutton and Silverman⁵⁹ determined the effect of 0.95 and 1.41% NaCl on the conductivity of a soda-lime glass, with results shown in Fig. 25. A satisfactory interpretation of such results is not possible with our present knowledge.

6. Dielectric Absorption in Glass.—Glass, in common with many dielectric materials, shows certain peculiarities in its electrical behavior which are generally referred to under the title of "Anomalous charging currents" or "Dielectric absorption."⁶⁰ So pronounced are these effects in glass that it is not surprising to find that it was probably the first material in which they were noticed, by Benjamin Franklin, who in 1748 described his observations on residual electrical charge in Leyden jars. The idea that the behavior is "peculiar" or the effects "anomalous" results from the observation that in this class of material the electric current which flows, under a given impressed voltage, is not a simple function of the temperature, the physical dimensions, and the conductivity of the sample, as is the case for the ordinary metallic or electrolytic conductors described by Ohm's law. Instead, in addition to the factors normally included in Ohm's law, the magnitude of the current flowing through the glass at any particular time is an undetermined function of the total elapsed time since the initial application of the voltage.

Because a dielectric such as glass at low temperatures cannot be made to act as a conductor of electricity without at the same time undergoing volume polarization, any system providing electrodes in contact with glass for the purpose of making conductivity experiments constitutes a condenser, as do any two conducting electrodes separated by a dielectric. In the ideal condenser of classical theory the application of a difference of potential to the plates

⁵⁹ M. Sutton and A. Silverman, *J. Am. Ceram. Soc.*, **7**, 86 (1924).

⁶⁰ For a summary and critical discussion of the theories of anomalous absorption currents in solids see lectures three to five inclusive (and extensive bibliography at end of book) in J. B. Whitehead, "Lectures on Dielectric Theory and Insulation," McGraw-Hill, New York (1927).

produces a sudden surge of electric charge from one plate to the other. This charging process is over in a very short interval of time which can be accurately expressed in terms of certain constant physical properties of the ideal condenser by a definite mathematical equation. If this charged ideal condenser is suddenly short-circuited by connecting together the plates, it discharges; its same physical properties once more serve to define the interval of time in which the process of discharge will be completed.

The behavior of an actual condenser in which the dielectric is glass, subjected to a similar charge and discharge cycle, may be contrasted to the ideal case as follows: Applying a difference of potential to the plates again produces a sudden surge of electric charge from one plate to the other. As this first surge due to the displacement current dies away, however, the flow of electric current into the glass condenser does not cease, as in the simple ideal condenser, but continues, the magnitude of this so-called anomalous charging current diminishing relatively slowly with time. This intermediate transient state of the charging current gives way in turn to a final steady state comparable to the conduction current in metals or electrolytes, though in general of a much lower order of magnitude. In this final stage the real condenser behaves as the ideal condenser might if a resistance, through which there would be a constant leakage current, were shunted across it. If the real condenser with glass dielectric be suddenly short-circuited, the discharge current, also, will differ in its behavior from the ideal condenser. The first impulsive rush of electricity is followed by a continued flow of current out of the glass, long after the displacement current of classical electromagnetic theory has died out. This so-called anomalous discharge current may be readily observed by removing the short-circuiting conductor and connecting the plates of the glass condenser to a sufficiently sensitive current-measuring device, which will indicate a reverse current coming out of the glass and following the

same undetermined law of variation as the anomalous charging current. Furthermore, the anomalous charging current in glass is reversible, so that not only does the discharge current resemble the charging current in its manner of variation in time but also its magnitude at any instant is that of the charging current, at the corresponding point in the charging cycle, diminished by the amount taken out by the final steady-state conduction current.

These same peculiarities in the electrical nature of glass may be examined in a different way by discharging a charged condenser, the dielectric of which is glass, and letting it stand for a short interval of time. Testing with a voltage detector then indicates that a potential difference has again established itself between the plates, and a so-called residual charge may be removed by again discharging the condenser. This process may be repeated several times before the absorbed charge is completely removed. This particular experiment is the one performed by Benjamin Franklin in 1748.

Since that time probably the most complete experimental investigation of dielectric absorption in glass was made by Hopkinson (1876-97). Among his numerous experiments in this subject, measurements of the above-mentioned residual charges in glass condensers after a succession of charges and discharges at irregular time intervals and polarities showed that anomalous charging currents and residual charges behave in accordance with the principle of superposition. Lord Kelvin is quoted by Hopkinson as saying, "The charges come out of the glass in the inverse order in which they go in." In Hopkinson's own words—"It seems safe to infer that the effects on a dielectric of past and present electric forces are superposable." This principle of superposition as exhibited in the behavior of anomalous charging currents in dielectrics such as glass may be stated as follows:

The variation in charging current resulting from several successive variations in the applied voltage is the

summation of the individual variations in charging current which would have taken place if each voltage variation had been separately impressed upon the uncharged condenser.

That this important principle applies to the behavior of dielectrics such as glass in which the absorption current is reversible has been confirmed by numerous investigators since Hopkinson's time, in particular by J. Curie, who studied the electrical behavior of a variety of substances. Curie and Wilson both found that changes in applied voltage or thickness of the dielectric do not affect the time

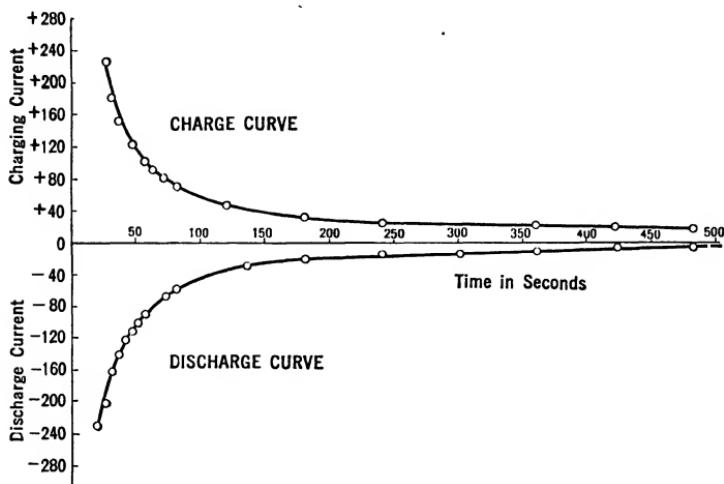


FIG. 31.—Typical Charge and Discharge Curve for a Borosilicate Glass.

rate of variation of the absorption current but only its absolute magnitude, which is proportional to the voltage gradient, as is the true conduction current. Increases in temperature, on the other hand, increase both the magnitude and the time rate of variation of the absorption current. Guyer,⁶¹ working at the Corning Glass Works Laboratory, has studied these various effects, and his results are given in Figs. 31, 32, and 33. Fig. 31 shows typical charge and discharge curves for a borosilicate glass. The

⁶¹ E. M. Guyer, private communication.

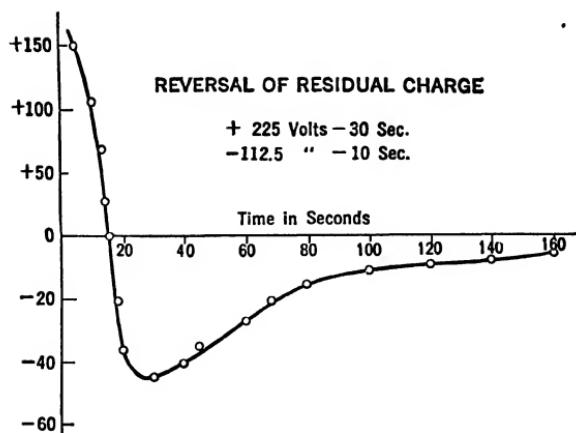


FIG. 32.—Reversal of Residual Charge in a Borosilicate Glass. The charging cycle is given in the figure; readings were taken after disconnecting the charging battery.

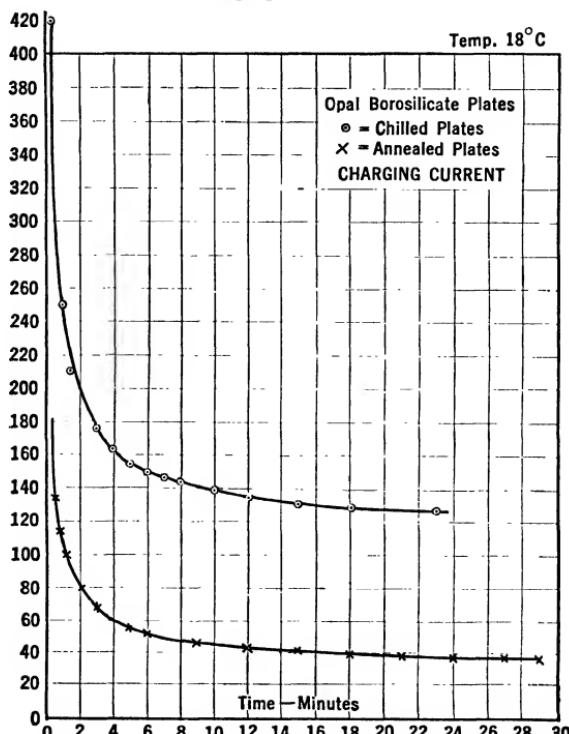


FIG. 33.—Effect of Chilling and Subsequent Annealing on the Charging Current in an Opal Borosilicate Glass.

discharge curve of Fig. 31 shows only the ascending branch of the curve, but the discharge curve of Fig. 32, made on a somewhat harder glass, shows the initial descending branch, followed by reversal of the direction of current flow. Fig. 33 shows the effect of annealing on the charging current.

An important implication of the principle of superposition, as it applies to the electrical behavior, is that the true electrical resistance, in the sense implied by Ohm's law, of glasses in which there is a purely reversible absorption current may be determined as follows: (1) Measurement of the current through the glass after successive intervals of time have elapsed since the initial application of voltage to the sample. (2) These data plotted as a function of the time give the characteristic charging curve of the glass under test. (3) A time-discharge current curve may then be plotted from data obtained by removing the applied voltage and observing the discharge current at successive times. (4) The differences in the magnitudes of the observed currents in the charge and discharge curves, respectively, for corresponding times will be constant in value for glasses in which the absorption current is purely reversible in character, and the current represented by this constant difference is the true conduction current through the glass. Should the differences, between the charging and discharging currents, at equal time intervals, fail to remain a constant, this would mean that the absorption current was not purely reversible and in consequence the conduction current could be separated from the absorption current only by repeating the measurements at many successive intervals of time until the current had ceased to vary. In some instances the variations continue for many hours.

Any measurements on the electrical resistance of glass⁶² at low temperatures are likely to be seriously in error unless the absorption current is taken into account, as

⁶² Cf. discussion, p. 64-66.

it may predominate over the conduction current. It is not sufficient to take measurements after a stated interval of time unless it has been previously shown that this time is sufficient to allow a complete decay of the absorption current.

In spite of the theoretical importance of this subject no complete study has been made of the absorption current in different glasses with the object of correlating this property with any known physical property or with composition. This may be due in part to the fact that there is no generally accepted adequate theory as to the nature of dielectric absorption.

Because more is known concerning the identity, mobility, and ionic nature of the electrical carriers in glass than in most solid dielectrics, and also, since the absorption currents in many glasses have a time rate of variation which may be measured in minutes and hours, thus falling within a range of time which permits convenient and accurate measurement, this material offers opportunities for needed research along two lines: firstly, correlation of variations in dielectric absorption with changes in physical properties (electrical and mechanical) throughout a series of glasses of systematically varied composition; secondly, a study, in the individual members of this series, of the effects of systematically varied physical factors on the behavior of the absorption current. Not only might such a study yield data leading to a better understanding of the phenomenon of anomalous absorption in glass, but these same data would undoubtedly throw more light on the structure and ultimate nature of glass itself.

CHAPTER III

DIELECTRIC CONSTANT

1. Introduction.—It has been shown by experiment that the charge Q on a conductor is proportional to V , the difference in potential between this conductor and the other conductors lying in the electrostatic field of this charge; that is

$$Q = CV \quad (1)$$

where C , a constant, is called the capacitance. The whole system of conductors and insulating media is called a condenser. C is dependent upon both the geometrical configuration and the material of the dielectric. If the capacitance of the condenser when the dielectric is a vacuum be C_v , and C the capacitance when a different dielectric is substituted for the vacuum, then

$$C = C_v K \quad (2)$$

where K is called the dielectric constant of the material. K for air at low voltages is 1.0006, or unity for practical purposes.

The magnitude of the dielectric constant of insulating materials is of considerable importance in the electrical industry. Usually, dielectrics of low dielectric constant are desirable, but in some instances materials with high values offer an advantage. Glasses are unique among solid dielectrics inasmuch as they present a range of dielectric constants varying by more than four to one.

A high dielectric constant is needed where maximum capacitance for a given size of condenser is desired, and under such conditions the total charge possible per unit of volume is a measure of the condenser value. The maxi-

mum charge obtainable depends upon the permissible voltage gradient, which in turn depends upon the minimum practical manufacturing thickness of the dielectric, the dielectric strength of the material, the change in properties with temperature, and the amount of dielectric heating due to conduction and displacement currents. Without going into any detail in regard to these properties, it can be stated that with the possible exception of mica, which can be obtained in very thin sheets, probably better condensers can be made from suitable glasses than from any other material, and where very efficient condensers are desired, glasses as dielectrics should certainly be investigated.

Materials of low dielectric constant are desirable for high-frequency insulation, for it has been shown that the power loss in an insulator in an alternating field is directly proportional to the dielectric constant. This will be discussed in more detail later.

Another advantageous application of material of low dielectric constant is in the usual high-voltage insulator. The stress on the air in series with the dielectric is proportional to the dielectric constant of the dielectric. This can easily be shown by the analogy to a parallel-plate condenser with two dielectrics in series, as is illustrated in Fig. 34. Let a be the thickness of the air film; b , the thickness of the dielectric or insulator of dielectric constant K ; V_1 , the voltage drop through the air; and V_2 , the drop through the insulator. V , the total voltage drop is $V_1 + V_2$.

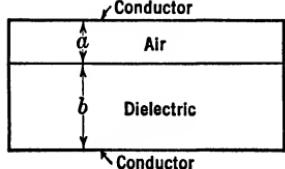


FIG. 34.

dielectrics in series, as is illustrated in Fig. 34. Let a be the thickness of the air film; b , the thickness of the dielectric or insulator of dielectric constant K ; V_1 , the voltage drop through the air; and V_2 , the drop through the insulator. V , the total voltage drop is $V_1 + V_2$.

$$V_1/V_2 = K(a/b) \quad (3)$$

or

$$V_1/a = KV_2/b \quad (4)$$

Now

$$V_1 + V_2 = V \quad (5)$$

Therefore

$$V_1 = V/[1 + b/(aK)] \quad (6)$$

and

$$V_2 = V/(1 + aK/b) \quad (7)$$

$$V_1/a = V/(a + b/K) \quad (8)$$

Let V_c = critical corona forming voltage gradient of air

$$V_1/a = V_c = V/(a + b/K) \quad (9)$$

Let a approach 0; then

$$V_c = VK/b \quad (10)$$

This shows that the smaller K is, the greater V will have to be before corona is formed, or before the air in series with the insulator is over-strained; in other words, the smaller K is, the smaller b can be to maintain a given air stress. Conditions in practice are of course not exactly similar to those in the parallel-plate condenser with uniform field and gradient, but the effect of the dielectric at any particular point or along any line of flux is similar to that in the illustration.

Very often insulating members of condensers are immersed in another dielectric, such as oil or wax, and it is desirable to have the dielectric constants of the two materials equal. If the oil or other material can be so selected as to have a value within the glass range of 3.7 to 16, it will be possible to make or select a glass to match the other material exactly.

The total line capacitance is affected by the insulator capacitance, but inasmuch as this part is only a small portion of the total capacitance, the material of the insulator has little practical effect. McMillan¹ has measured the added capacitance due to the insulators on a line con-

¹F. O. McMillan, "Radio Interference from High Voltage Insulators," Report of Engineering Section of Northwest Electric Light and Power Association, March, 1930, p. 181.

structed of 7-strand 133,000-c.m. copper conductors, with 7 ft symmetrical triangular spacing, and having both standard 20 and special 30 micro-microfarad capacitance insulators.

The effect of the insulators is shown in the table.

Pole Spacing	Per Cent Capacitance Conductor Alone	Per Cent Capacitance Conductor and Standard Insulation	Per Cent Capacitance Conductor and Special Insulation
150	100	104.7	106.7
200	100	103.5	105.3
250	100	102.8	104.2
300	100	102.3	103.5

The insulator capacitance will be relatively higher when the insulators are wet. However, it is evident that only a slight and probably a negligible change in total line capacitance can be effected by changing the dielectric constant of the insulator material.

As a research material for the development or test of dielectric theories, glass offers a variety of compositions and properties, which to a certain extent are separately alterable.

2. Early Measurements of the Dielectric Constant of Glasses.—Hopkinson² in 1878 made measurements on several glasses and found that the dielectric constant varied from 6.57 for "very light flint" to 10.1 for "double extra dense" flint. He further observed for the same glasses, where K is the dielectric constant and s the density, that

$$K/s = 2.2 \text{ approximately}$$

K was found to be constant up to gradients of 50 kv per cm and did not vary greatly with frequency. K increased by a factor of 2.6 as the temperature was raised

² J. Hopkinson, Phil. Trans., (1) 17 (1878). Proc. Roy. Soc. London, 355 (1881).

from 25° to 170° C with a frequency of 85 cycles; at 2×10^6 cycles the capacity was not affected by this temperature range; and at 8400 cycles the change was still very small. Hopkinson ascribed the effect at low frequencies to residual charge.

The work since Hopkinson's experiments has been mostly an extension of his experiments to many additional glasses. Much of this work has been summarized in Tables 13 and 21.

3. Dependence of Dielectric Constant on Frequency.—The Maxwell equations for the electromagnetic wave propagation lead to the relation $n^2 = K$, where n is the index of refraction of the medium, and K is the dielectric constant. This equation, of course, assumes n and K to be measured for the same frequency. Comparison of the validity of this relation is frequently incorrectly made where n is measured for visible light and K for either d-c voltage or low frequencies.

The reflecting power R of a homogeneous isotropic material according to the Maxwell equations is given by $R = (n - 1)^2/(n + 1)^2$, and if $n^2 = K$ then K can be determined by measurements of R . This was done by Rubens,³ who found that the values of R computed from measurements of K agreed very closely with the measured values. Rubens tested crystalline quartz and silica glass, ebonite, and a series of twelve glasses where K varied from 5.61 to 16.2.

Addenbrooke⁴ compared the density with n^2 and K at a frequency of 150 cycles per second for seven glasses and found that K/n^2 (where n is the index of refraction for sodium light) varied from 2.75 to 3.55 and K varied from 6.57 to 13.0. n^2 for this latter glass has the value of 3.68. This means that K changes from 13.0 at a frequency of 150 to 3.68 at a frequency of 5×10^{14} cycles; consequently the change in K in the radio-frequency band should be very small.

³ H. Rubens, Sitzber. kgl. preuss. Akad. Wiss., 1916, II, 1280.

The measurements cited later show this to be the case. Addenbroke's data are given in curves in Fig. 35. The results on Pyrex chemical resistance glass are also shown in the figure. When these results are considered, the straight line which Addenbroke⁴ draws through the $K = 1$ point is somewhat displaced.

The measurements on crystalline and fused quartz at various frequencies have been collected by Sosman.⁵

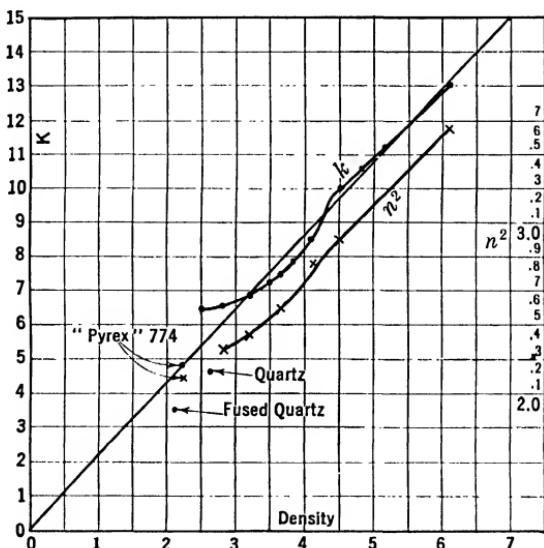


FIG. 35.—Variation of K and n^2 with Density.

The results are given in Table 17.

There appears to be very little if any effect of frequency change where frequency has been varied by a factor of 10^5 .

The data obtained by Rubens⁶ and Jaeger⁷ on a series

⁴ G. L. Addenbroke, Phil. Mag., **45**, 516 (1923).

⁵ R. B. Sosman, "Properties of Silica," Chemical Catalog Co., p. 516 (1927).

⁶ H. Rubens, Sitzber. kgl. preuss. Akad. Wiss., **38**, 556-567 (1917).

⁷ R. Jaeger, Ann. Physik, (4) **53**, 409 (1918).

TABLE 17

DIELECTRIC CONSTANTS OF SILICA AS MEASURED BY DIFFERENT METHODS
Jaeger (1917)

	Quartz Plate Perpendicular to Axis			
	14	15	16	(Mean of 14, 15, 16)
Specimen No.	14	15	16	(Mean of 14, 15, 16)
Thickness, mm.	1.930	2.003	2.010	
K by method I.		4.32	4.43	4.38
K by method II.	4.40	4.41	4.41	4.41
K by method III.	4.40	4.37	4.40	4.39
K by method IV.		4.34	4.43	4.39
K by method V.	4.695			4.70
K by method VI.		4.65		4.65
Mean of two groups of methods *				4.58
	Vitreous Silica			Wave-length, Meters
		Frequency		Wave-length, Meters
Specimen No.	12	13	(Mean of 12 and 13)	
Thickness, mm.	2.027	1.909		
K by method I.	3.66	3.69	3.68	250 (1 to 2) $\times 10^6$
K by method II.	3.61	3.71	3.66	10 ⁵ 3000
K by method III.	3.58	3.59	3.59	10 ⁶ 300
K by method IV.	3.57	3.56	3.57	10 ⁷ 30 to 40
K by method V.	3.80	3.80	3.80	3 \times 10 ⁷ 10
K by method VI.	3.72		3.72	10 ⁵ 3000
Mean of two groups of methods *			3.72	

* The mean of methods V and VI is given double weight as compared with the mean of methods I to IV. The values differ a little from the values published by the author, as there seem to have been some errors of transcription in his summarized table.

of glasses are given in Table 18. n_D is the index of refraction for sodium light.

It is evident from these data that K for most glasses

TABLE 18

	Type	Dens- ity	n_D	Dielectric Constant for			
				3000 m	10 m	57 mm	0.3 mm
Clear Plate Glass.....		2.54	1.5301	7.16	7.10		
Black Glass.....		2.69	1.5504	7.41	7.31		
Violet Glass.....		2.53	1.5341	6.85	6.89		
Fluoride Crown, O 7185.....	464/656	2.27	1.4637	5.84	5.78	5.64	5.54
Phosphate Crown, S 367.....	516/640	2.59	1.5164	6.41	6.40	6.28	6.17
Uviol Crown, UV 3199.....	504/644	2.41	1.5035	5.66	5.56		
Crown with higher dispersion, O 381 (O 2074).....	526/513	2.70	1.5262	6.95	6.90		
Heavy Barium, O 1209 (O 1993).....	611/572	3.55	1.6112	8.19	8.21		
Medium Barium, O 1266 (O 1353).....	604/494	3.50	1.6042	7.68	7.73		
Medium Flint, O 118 (O 2051)	613/369	3.58	1.6129	7.52	7.42	7.33	7.37
Heavy Flint, O 255.....	717/295	4.46	1.7145	9.98	9.55	9.41
Lead Silicate, S 461.....		6.01	1.9170	16.3	16.1	15.6	15.6

decreases only a very small amount with increasing frequency.

Schott⁸ finds a slight decrease of K with increasing frequency in some glasses, the maximum observed change in K being a decrease of about $\frac{1}{2}\%$ as the frequency was changed from 1.9×10^5 to 10^6 cycles. MacLeod⁹ reports a $4\frac{1}{2}\%$ decrease in K as the frequency was varied from 500 to 10^6 cycles. His measurements were made on two lime glasses and on Pyrex chemical resistant glass.

4. Effect of Temperature on Dielectric Constant.—This effect has been investigated only to a very limited extent over a small range of temperature.

Gray and Dobbie¹⁰ measured K for a series of eight glasses at two different temperatures.

⁸ E. Schott, Z. drahtl. Tel., **18**, 82-122 (1921).

⁹ H. J. MacLeod, Phys. Rev., **21**, 53 (1923).

¹⁰ A. Gray and J. Dobbie, Proc. Roy Soc. London, **63**, 38-44 (1898); **67**, 197 (1901).

The data are given in Table 19.

TABLE 19

Glass Type	Temperature, Degrees C.	K	Density
Soda-lime.....	11	6.26	2.487
	129	6.79	
Soda-lime-didymium.....	22	6.93	3.11
	147	7.18	
Soda-potash 26% PbO.....	10	7.06	2.99
	130	7.90	
Soda 39% PbO.....	19	7.376	3.36
	130	7.44	
Soda 40% PbO.....	20	8.013	3.408
	140	7.302	
Potash 40% PbO.....	18	6.766	3.34
	140	7.05	
10.6 Potash 41% PbO.....	18	7.22	3.41
	140	7.42	
13.7 Soda 45% PbO.....	8	5.42	3.552
	130	5.69	

A glass having the composition SiO_2 33%, Al_2O_3 6%, B_2O_3 12%, BaO 48% had a value of K equal to 8.5 which did not change with temperatures up to 140° C.

Strutt¹¹ has measured the effect of temperature on K for five glasses at different frequencies. Three of the curves obtained by Strutt are reproduced in Fig. 36. Glass 1 is a borosilicate glass probably similar to Pyrex chemical resistant glass; 4 is a soda-lime glass of about 70% SiO_2 and 16% Na_2O ; and glass 5 is "heavy lead glass."

These curves show that for each frequency the dielectric constant increases with increasing temperature, and in the case of low frequencies the displacement current rapidly becomes masked by the conduction current. Glass 1 should have a much higher electrical resistance than the other glasses, and this should be relatively less affected

¹¹ M. J. O. Strutt, Arch. Elektrotech., 25, 715 (1931).

by temperature. The data show this to be the case. At higher frequencies K is not affected by temperature to the same extent as at the lower ones.

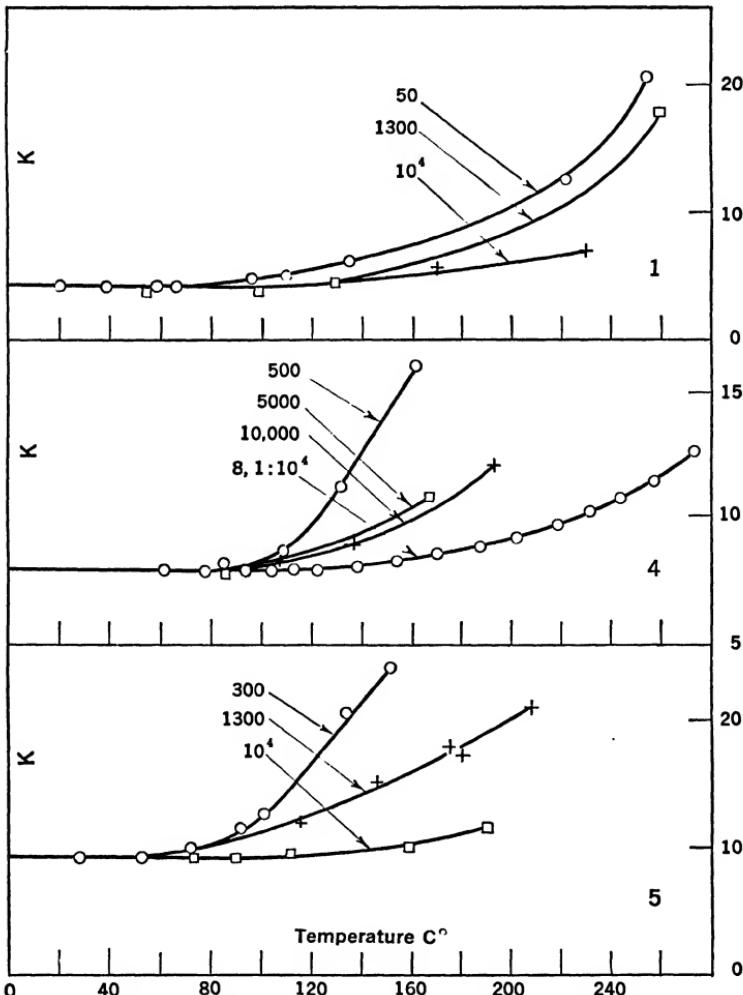


FIG. 36.—Dependence of K on Temperature at Various Frequencies. After Strutt.

The practical question as to the maximum operating temperature for a glass condenser accordingly depends upon both the composition of the glass and the frequency. For

low frequencies about 80° C approximates the limit of stability for lime glasses and 120° C for the borosilicate type; for frequencies of the order of 10^4 cycles lime glass is practically constant up to 140° C and the borosilicate type to 240° C.

Leyden jar condensers have been frequently operated at high temperatures, but there seems to be no record of the temperatures obtained in such experiments. If, however, constant capacity is desired the temperature should be kept below the limits cited above. Electrical failure caused by temperature rise is primarily a conductivity phenomenon, but the increase of K with temperature is a contributing cause to the temperature instability.

CHAPTER IV

DIELECTRIC LOSS

1. Introduction.—When an alternating current I flows into a condenser charging it to a potential V , the power loss P is given by the equation

$$P = VI \cos \theta \quad (1)$$

where θ is the phase angle (Fig. 37).

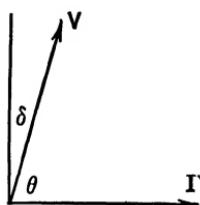


FIG. 37.

In most commercial dielectrics, θ differs from 90° only by a small amount. If, instead of the phase angle θ , the phase difference angle δ or $(90^\circ - \theta)$ is used, we have

$$P = VI \sin \delta \quad (2)$$

and hence

$$\sin \delta = P/VI \quad (3)$$

$\sin \delta$ is then the power factor, that is, the ratio of the power loss to the total power flowing. For small angles

$$\sin \delta = \tan \delta = \delta \text{ (in radians) approximately}$$

Various authors express power factor in different ways, some as phase difference angle in degrees or minutes, and others as $\tan \delta$, $\sin \delta$, δ or power factor, and per cent power factor. Numerically for small angles, power factor in per cent is 1.745 times the phase difference angle in degrees.

However, power factor is not the only material constant that has to do with the dielectric absorption of power. The following evaluation of power loss is from Hoch.¹ For small loss angles

$$P = VI\delta \quad (4)$$

¹ E. Hoch, Bell System Tech. J., 1, 110 (1922).

and

$$I = 2\pi fVC \quad (5)$$

where f is the frequency and C the capacitance.

Let

$$C = aK \quad (6)$$

where a is a constant and K the dielectric constant. Consider a parallel-plate condenser where A is the area of one plate and d the distance between the plates. Then

$$a = mA/d \quad (7)$$

where m is a constant depending upon the units chosen. Therefore

$$P = 2\pi fV^2aK\delta \quad (8)$$

Hence

$$P/(Ad) = 2\pi fm(V/d)^2K\delta \quad (9)$$

The power loss per unit volume of the material is therefore proportional to the frequency, the square of the voltage gradient, and the product of δ and K . This shows that not δ alone but rather the product of δ and K should be used as a measure of the dielectric loss of the material.

The loss in watts per second per unit volume of a parallel-plate condenser is

$$P_v = P/(Ad) = 2\pi fm(V/d)^2K\delta = 5.55 \times 10^{-13}f(V/d)^2K\delta \quad (10)$$

when δ is power factor, V is in volts, and d is in centimeters.

If the frequency be 1,000,000 cycles per second and the voltage gradient 10 kv per cm, the product δK , when δ is expressed in degrees, is approximately equal to the dielectric loss in watts per cubic centimeter.

For power-transmission-line service the dielectric loss of the insulators is so small that it is negligible, and the difference in loss between the various possible insulating materials is of no consequence. With high-frequency currents, however, this loss in the material is of considerable importance, and it is desirable to select insulation having

a low dielectric loss factor. An evaluation of that percentage of total loss which is due to dielectric absorption of telephone insulators operating at a frequency of 30,000 cycles has been made by Wilson.² Wilson concluded that the difference between possible insulators might amount to a saving of about 6% of the total loss. The different glasses studied by him varied in dielectric loss by a ratio of 20 : 1. As the other line losses are decreased by design and installation changes the dielectric loss increases relatively to the total line loss, and the insulating material used becomes increasingly important.

For high-voltage high-frequency condensers it goes without saying that low-loss materials should be selected. If a high capacity is desired a material having a high dielectric constant furnishes this desired capacity with a smaller condenser volume, but the power loss per unit of volume is increased in proportion to the dielectric constant. If the voltage and frequency conditions are severe, then a material having both a low dielectric constant and a low power factor should be chosen, as this provides a lower energy absorption per unit volume and makes possible a greater area for energy dissipation.

Two general classes of glass are available, those having a high K and low δ value and those having both K and δ low, K and δ being separately alterable by changes in the glass compositions. A tabulation of the measurements of δ and K for different glasses is given at the end of this section.

2. Accuracy of Measurements.—Measurements of small power-factor values are made with considerable difficulty, since the loss in such glass condensers is so small that stray losses in the circuit have a large effect. The authors have power-factor data from different laboratories on samples of the same glass, and the deviation in values is quite large. This will be referred to in more detail later on. Accordingly, it is believed that the

² L. T. Wilson, Trans. Am. Inst. Elec. Engrs., 49, 1536 (1930).

absolute values of the power factors of the extremely low-loss glasses are not known with a great deal of certainty. The relative values of power factor for high-loss glasses where the data are obtained on the same equipment are probably fairly exact, but in low-loss glasses where a constant error has a greater effect, even relative values are not dependable. It appears that data from different laboratories are not always comparable, and to be trustworthy measurements should be made by the various laboratories on the same glass as a check. Compositions of the glasses measured are not usually given with sufficient exactitude to serve as a guide for comparison of loss measurements.

3. Effect of Frequency on Power Factor.—Von Schweidler³ deduced the equation

$$i = VC_0 B t^n \quad (11)$$

where i is the residual charging current, V the constant impressed electromotive force, C_0 the capacity at infinite frequency, t the time, and B and n constants with n lying between zero and one. If

$$V = V_0 \sin \omega t \quad (12)$$

where ω is the frequency in radians per second, and if the conduction loss be neglected in comparison to the dielectric absorption, the equation for the power loss is

$$P = \text{constant} \times V^2 \omega^n \quad (13)$$

This is deduced from the original equation by substituting in the equation for i the proper values of the conduction current, the charging current, and apparent capacity.

The power loss for a constant voltage is then a function of frequency expressed by the equation

$$P = B f^n \quad (14)$$

where f is the frequency in cycles per second and B a

³ E. R. von Schweidler, Ann. Physik, 24, 711 (1907).

constant. The terms in this equation can be evaluated by measurements of P at various frequencies.

n can also be evaluated by measurements of the change in capacity with frequency, as it may be deduced from the von Schweidler equation that

$$C = C_0[1 + M/f^{(1-n)}] \quad (15)$$

This expresses the capacitance as a function of frequency.

In agreement with the von Schweidler equation,

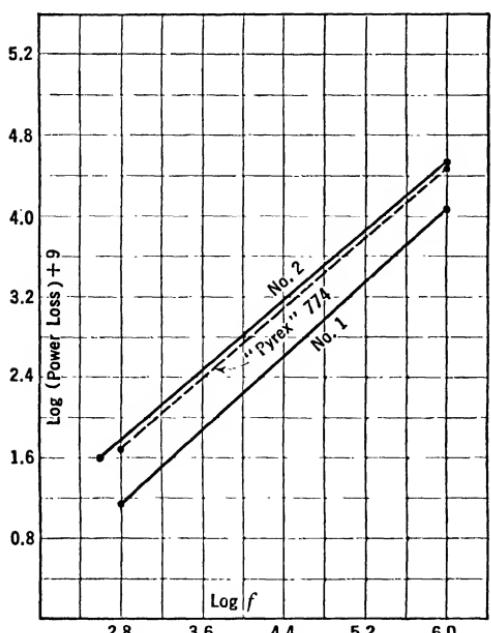


FIG. 38.—Power Loss-Frequency. After MacLeod.

loss is for unit voltage. These data are consequently in agreement with equation (14). The power factor is also equal to $R\omega C$, and the power loss $P = V^2R\omega^2C^2$, where R is the equivalent series resistance of the condenser as measured.

⁴ H. P. Lawther, Thesis, Harvard University (1916).

⁵ H. J. MacLeod, Phys. Rev., 21, 53 (1923).

Lawther⁴ found that the power loss in condensers of mica and glass was represented by equation (14). MacLeod⁵ studied three glasses at frequencies from approximately 500 cycles to 1,000,000 cycles. He found the power factor to decrease by a factor of from 2 to 3 as the frequency increased over this range.

The results for the three glasses are shown in Fig. 38, where the power

MacLeod's data showed that R varies with f according to the equation:

$$R = A/f^k \quad (16)$$

These two experimental equations lead to the relation

$$\delta = D/f^{(t-n)/2} \quad (17)$$

which, if D , k , and n are known, allows δ to be computed for any f . The values of k , n , and D for the three glasses are as follows:

	k	n	D
Glass 1.....	1.095	0.90	0.00714
Glass 2.....	1.13	0.86	0.0373
Pyrex chemical resistant glass.....	1.15	0.885	0.0264

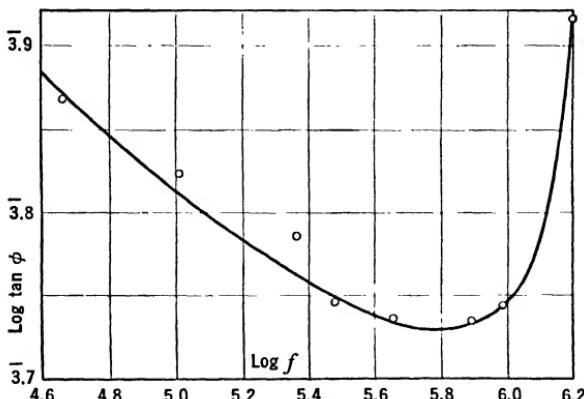


FIG. 39.—Power Loss-Frequency. After McDowell and Begeman.

McDowell and Begeman,⁶ using a series of six glasses, studied the change of power factor with frequency. The frequency range covered was from 800 to 4000 cycles, except for one glass, where measurements were made to 1500 kc. They found that, for frequencies from the audio range up to 100 to 200 kc, the von Schweidler equation was valid; but above 700 kc the power factor of their No. 1 glass passed through a minimum. Above this point, the

⁶ L. S. McDowell and H. L. Begeman, Phys. Rev., 33, 55 (1929).

power factor rapidly increased. This change is shown in the curve, Fig. 39.

The values of n obtained for frequencies up to 4000 cycles agreed very well with the values of MacLeod, though they are somewhat higher than those of Tank⁷ and von Schweidler.³

Decker⁸ measured a series of eleven glasses at frequencies of 10^3 and 3×10^4 . All glasses showed a decided decrease in power factor as the frequency was increased.

Schott⁹ made some measurements on three glasses which showed a power factor decreasing with increasing frequency. His "S" glass at "low frequency" (probably 55 cycles) was measured by Cohn and had a $\delta = 0.0195$. The Schott measurements are given in Table 20, and show that at 1.87×10^5 cycles $\delta = 0.0054$ decreasing to 0.0051 at 6×10^5 cycles. The value of δ for the Schott glass 0381 changes from 0.00755 to 0.00635 as the frequency is changed from 1.87×10^5 to 6×10^5 cycles.

The data cited all show a decrease of power factor with increase in frequency except for the McDowell and Begeman glass No. 1 which showed a reversal at 7×10^5 cycles. However, there are other measurements on other glasses which show the opposite effect. The glasses 0211, 015, and T163, as measured by Schott, showed the power factor to increase in the frequency range of 1.87×10^5 to 4.3×10^5 cycles.

Möller¹⁰ gives data on two glasses and also on quartz. The Möller results are shown in the curves of Fig. 40.

Strutt¹¹ obtained very erratic results at room temperatures. At temperatures above 100°C he found the power factor always to decrease as frequencies were varied from 50 cycles to 300 kc. His glass No. 1, which he called a

⁷ F. Tank, Ann. Physik, **48**, 307 (1915).

⁸ W. C. Decker, Elect. World, March 19 (1927).

⁹ E. Schott, Jahrb. drahtl. Tel., **18**, 82 (1921).

¹⁰ E. Möller, Arch. Elektrotech., **15**, 16 (1926).

¹¹ M. J. O. Strutt, Arch. Elektrotech., **25**, 715 (1931).

"Pyrex type," ¹² gave the following values as taken from his curve at 20° C.

Frequency.....	50	160	500	1300	10,000
Power factor.....	0.0031	0.0018	0.002	0.0027	0.0040

These results indicate a very rapid change between frequencies of 50 and 160. No one else has observed any

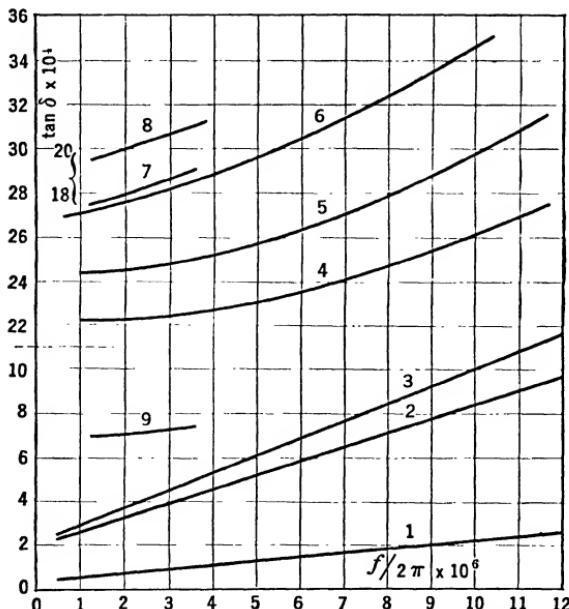


FIG. 40.—Power Factor-Frequency. After Möller.

1. Crystal Quartz	5. Alkali-Free Glass 41° C
2. Schott .0103 -20° C	6. Alkali-Free Glass 64° C
3. Apparatus Quartz	7. Data by Schott 015 Glass
4. Alkali-Free Glass 20° C	8. Data by Schott T163 Glass
9. Data by Schott 0211 Glass	

such abnormality in this zone. This is possibly due to some experimental error which is relatively larger with respect to actual power-factor values in the low-temperature low-loss zone, but which becomes relatively unimportant at higher temperatures where the dielectric losses are much greater.

¹² This term probably means a glass of the characteristics of Pyrex chemical resistance glass.

In order to demonstrate the large discrepancies between the measurements of different observers the different data on Pyrex chemical resistant glass have been collected, and curves between power factor and log frequency are shown in Fig. 41. Where the data have been published, the author's name accompanies the curve. The other values are from unpublished laboratory reports. It is evident

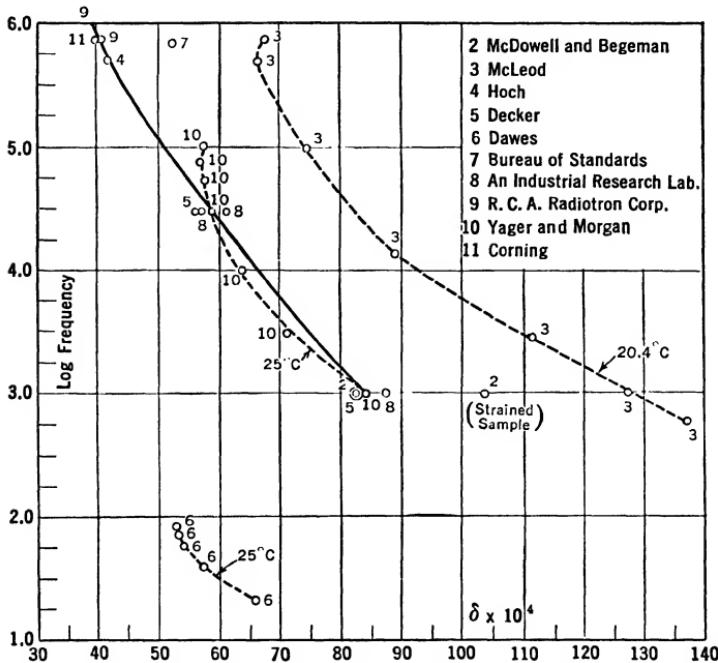


FIG. 41.—Power Factor-Frequency. Pyrex Chemical Resistant Glass. Data from Various Laboratories.

that the agreement is very poor. McDowell and Begeman¹³ obtained values for strained glass almost twice that of annealed glass, so that possibly the state of annealing in the samples measured may account for a part of the difference between the results of the various observers. However, since the majority of the measurements have

¹³ L. S. McDowell and H. L. Begeman, Phys. Rev., **31**, 476 (1928).

been made on stock samples having good commercial annealing, variations in annealing can account for only a very minor part of the discrepancies in the results. The discrepancies cannot be due to slight changes in chemical composition of the different samples. Unpublished measurements from the Corning Glass Works Laboratory show that a considerable variation in the composition of the given glass is required to cause the changes in the power factor of the magnitudes shown. Composition tests much more sensitive than power-factor measurements indicate no appreciable difference between the various samples of the glass used in the power-factor tests. Check measurements have also been made on the glass by different laboratories over a period of years, and although the laboratories do not check one another they always reproduce their own measurements within less than 10%. Also, some of the measurements reported by different laboratories were made on the same sample of glass.

The only conclusion to be drawn from these results is that in some glasses the power factor increases with frequency and in other glasses it decreases with frequency, with possible inversion points at frequencies above those of the measurements. It is possible that some of the measurements at the higher frequencies have been complicated by the heating of the dielectric, which has resulted in an apparent increase in the power factor.

The general conclusion is that the experimental error in the measurement of low-loss glasses is very often quite appreciable, and that the comparison of data from different laboratories cannot safely be made, even though the measurements be made on the same glass. In addition to the question of the accuracy of the measurement, there is also that of accurate knowledge of the chemical composition of the glasses measured. Unless this be known a comparison of results by different observers is impossible. Probably differences in results between the different experimenters would have been more in evidence had the

compositions of the glasses been published with the power-factor measurements.

There is certainly room for further research in this field.

4. Variation of Power Factor with Field Strength.—

The question as to the variation of δ with the voltage gradient has been little investigated. Equation (9) gives the loss per unit volume and holds for the values of K and δ for the given V/d of the equation. However, Moscicki¹⁴ in his experiments on high-voltage condensers found that δ depends upon V/d as well as f . He found that:

$$\delta = m(V/d)^\alpha f^B \quad (18)$$

and therefore

$$P/(Ad) = 2\pi f^{(B+1)} m(V/d)^{(\alpha+2)} K \quad (19)$$

where

$$0 < \alpha < 1 \quad \text{and} \quad 0 < B < 1.$$

The power factor therefore increased with increasing V . Moscicki used "Bohemian test tube glass" with voltage gradients as high as 1.3×10^6 volts per cm.

On the contrary, Dawes and Humphries¹⁵ reported that up to 3.54 kv per cm δ did not depend upon the voltage. Inge and Walther¹⁶ reported that Mandryka found no change in power factor up to field strengths of 1.15×10^6 volts (effective) per cm.

Inasmuch as the total power loss depends upon the square of the voltage gradient, the dielectric heating will depend upon the square of the voltage gradient and the time of application of the voltage. The difference between the results of Moscicki on the one hand and Dawes and Mandryka on the other can possibly be explained by the difference in the heating that might have occurred.

5. Effect of Temperature on Power Loss.—The variation of power factor with the temperature is of interest for both practical and theoretical reasons. Power factor

¹⁴ J. Moscicki, Elektrotech. Z., **25**, 527 (1904).

¹⁵ C. L. Dawes and P. H. Humphries, Elec. World, **91**, 1331-2 (1928).

¹⁶ L. Inge and A. Walther, Arch. Elektrotech., **22**, 410 (1929).

increases rapidly with rise in temperature, resulting in an increasing rate of energy absorption. As the temperature increases the dielectric heating increases, and eventually the system becomes unstable and breakdown occurs. This effect is of importance only in the case of high field strengths with the very high-frequency ranges, since only under such conditions is it possible for reasonably good dielectrics to reach the temperature of unstable equilibrium. In other cases, of course, it may be necessary to use the dielectric at elevated temperatures, and under such conditions it is essential to have some information as to the changes in the properties of the dielectric with temperature. The study of temperature effects is also of considerable theoretical significance. The application of such data to the development of dielectric theory has been of major interest to the workers in this field, and consequently the obtaining of what may be called engineering data has been neglected.

Schott,⁹ McDowell and Begeman,⁶ and Strutt¹¹ have discussed the relationship between electrical conductivity and power factor. The general conclusions are that at the lower temperatures power loss is due to a true dielectric loss with very little effect due to the ohmic resistance of the glasses, whereas at higher temperatures the resistance of the material decreases to such an extent that the conduction current is predominating.

The results of Schott⁹ on one glass are given in Fig. 42.

The curves show that the loss angle begins to increase fairly rapidly after the temperature of 100° C is reached, and at 340° C it has increased to about 40 times the value at 20° for a wavelength of 1600. Schott⁹ also made measurements down to -80° C and found a continual decrease of power factor with decreasing temperature even in these lower temperature ranges. The resistance curve (Fig. 43) for this same glass shows how rapidly resistance changes with temperature, but there is no exact relationship between the power factor and specific resistance. An increase in

frequency or temperature caused a decrease in specific resistance whereas power factor increased with increasing temperature and decreased with increasing frequency.

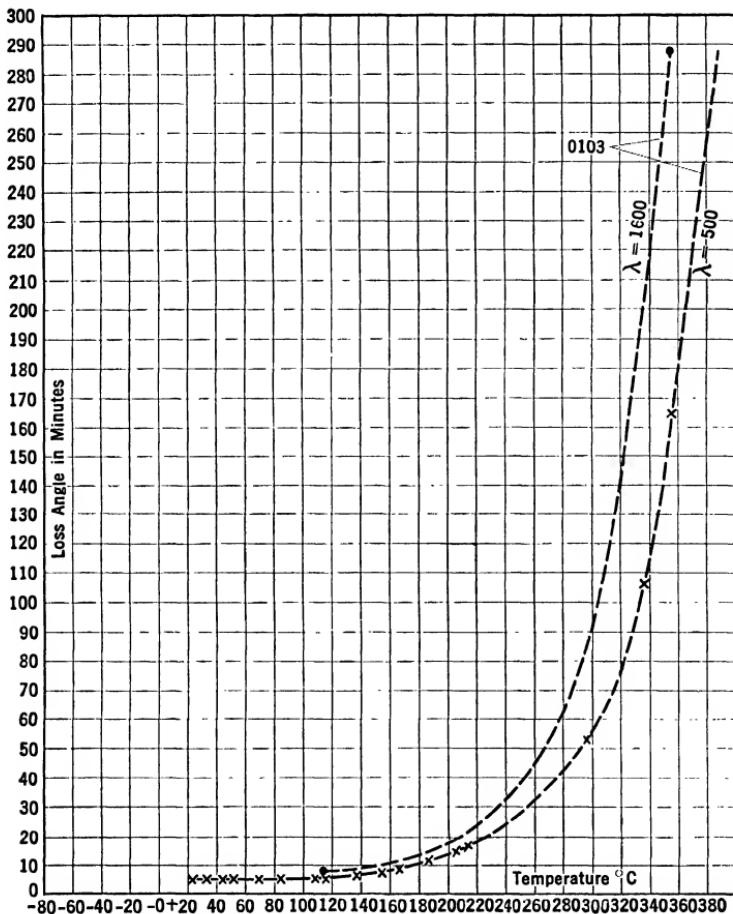


FIG. 42.—Loss Angle-Temperature. After Schott.

The two properties therefore did not vary alike as temperature and frequency changed.

McDowell and Begeman^{6,13} studied the effect of change in frequency on power loss for six glasses at several constant temperatures, and the effect of change in tempera-

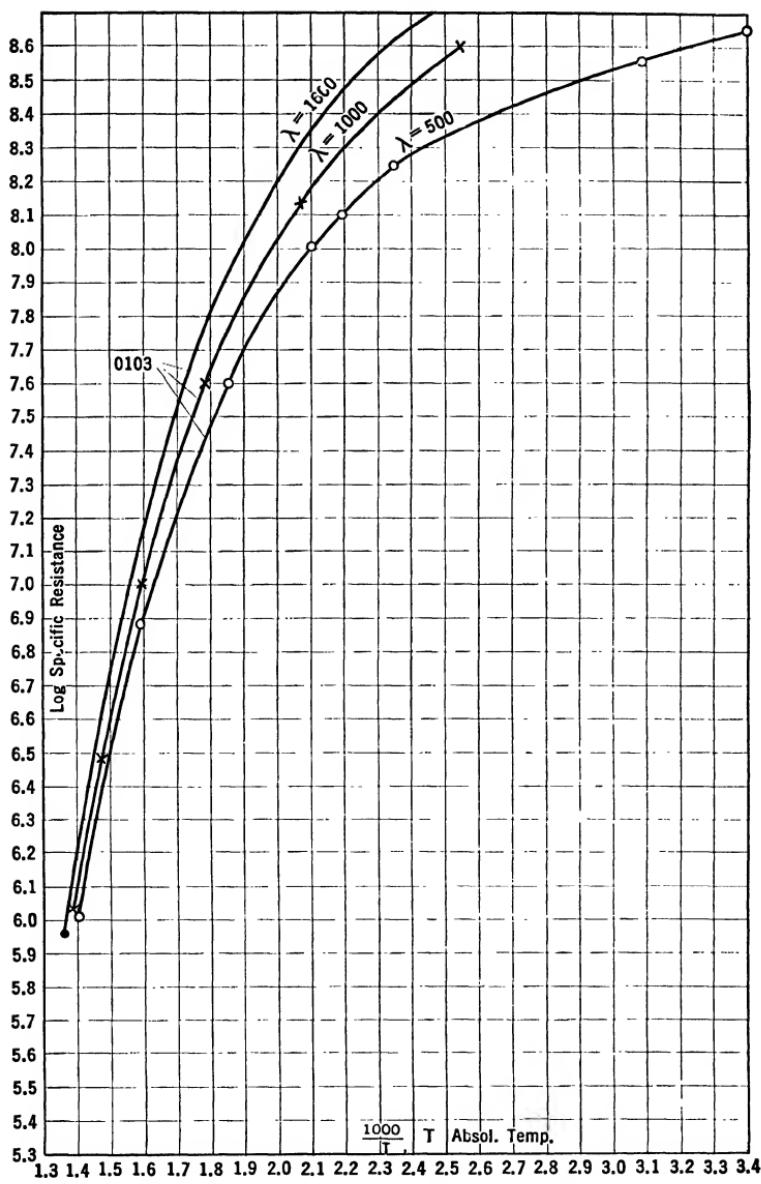


FIG. 43.—Specific Resistance-Temperature. After Schott.

ture in the case of one glass over the range from 20° to 160° C and also at -186° C. Resistance measurements were made at temperatures from 20° to 500° C and were found to follow accurately the Rash and Hinrichsen

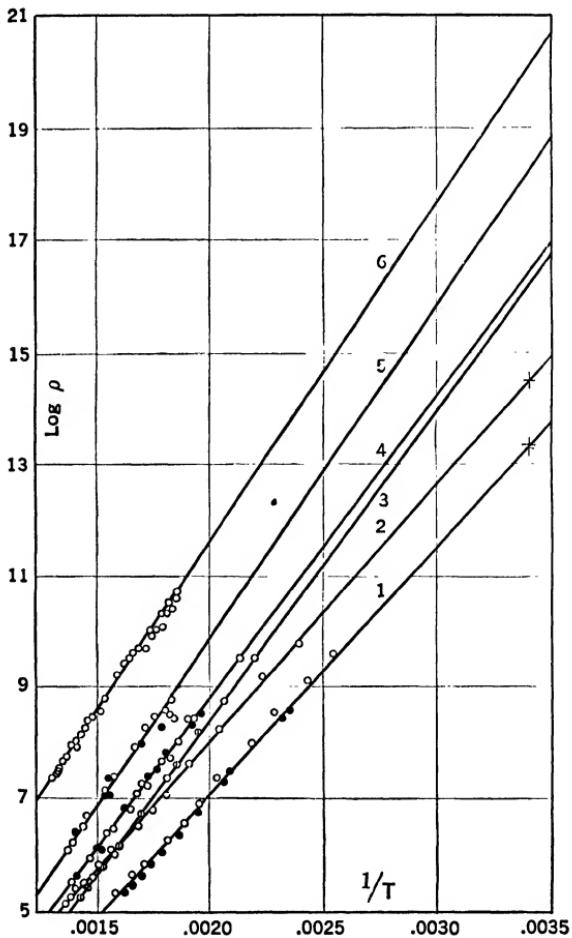


FIG. 44.—Specific Resistance—Temperature. After MacLeod and Begeman.

equation, $\rho = e^{k/T}$, where ρ is the specific resistance and T is the absolute temperature. The measurements on specific resistance are shown in Fig. 44. These measurements were made at a frequency of 1000 cycles. It is to

be noted that the curves differ considerably from those of Schott⁹ given in Fig. 42.

The comparison between power factor at 1000 cycles and specific resistance at 20° C is given in Table 21.

TABLE 20

Glass	ρ (20° C.)	Power Factor
1	2.3×10^{13}	0.0132
2	3.1×10^{14}	0.0082
3	2.0×10^{15}	0.0031
4	2.5×10^{15}	0.0039
5	3.5×10^{16}	0.00077
6	8.1×10^{19}	0.0022

Glass 6 has the highest resistance and glass 5 the lowest power factor. Except for glass 6, power factor decreases as the resistance increases. The resistance is entirely too high to account for the power loss. Power factor at room temperature, computed from the conduction current, is negligibly small in comparison with the measured value.

Power factor increases with temperature owing both to the increase of the conduction current and to the increase of the absorption current. McDowell and Begeman⁶ were able to correct their power-loss measurements for the portion due to conductivity. Their results on glass 2 are given in Fig. 45.

The corrected values of $\tan \delta$ are given by

$$\tan \delta = A e^{0.0077T}$$

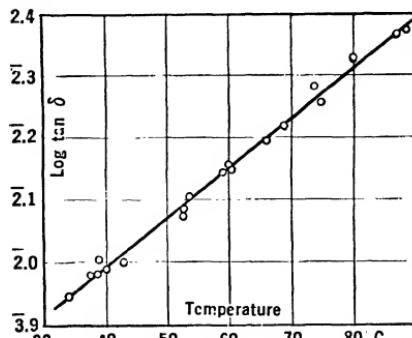


FIG. 45.—Power Factor (Corrected for Conduction Loss)—Temperature. After McDowell and Begeman.

This equation did not hold for liquid-air temperatures, as $\tan \delta$ measured 0.0015 at -186° and from the equation should be 0.00021. The authors concluded that this difference was due to the strain introduced by the rapid cooling. They believed this conclusion to be further justified by the fact that power factors measured for increasing temperatures, beginning with liquid-air temperatures, were consistently higher than those for decreasing temperatures, and the repeat measurement at room temperature was considerably higher than the original measurement, being more nearly the value obtained for strained glass. This conclusion, however, cannot be true, for it would be impossible to permanently strain glass the required magnitude at such low temperatures. The only strains possible would be of a temporary nature due to a temperature gradient in the glass at the time of measurement, and it is presumed that constant temperature was maintained long enough for uniformity to be attained before making the measurement.

Strutt¹¹ found a linear relationship between $\log \tan \delta$ and T as did McDowell and Begeman for their corrected values of $\tan \delta$. He further verified this relationship for the different frequencies, and his conclusions agree with Schott's⁹ in that the power factor increases with temperature more rapidly for low frequencies than it does for the higher ones. The curves of Strutt¹¹ are reproduced in Fig. 46.

Hoch¹ gives data on Pyrex chemical resistance glass as follows:

Temperature	<i>K</i>	δ	$K\delta$
20	4.9	0.0042	206×10^{-6}
74	5.0	0.007	350
125	5.0	0.0122	610
19	4.9	0.0044	216

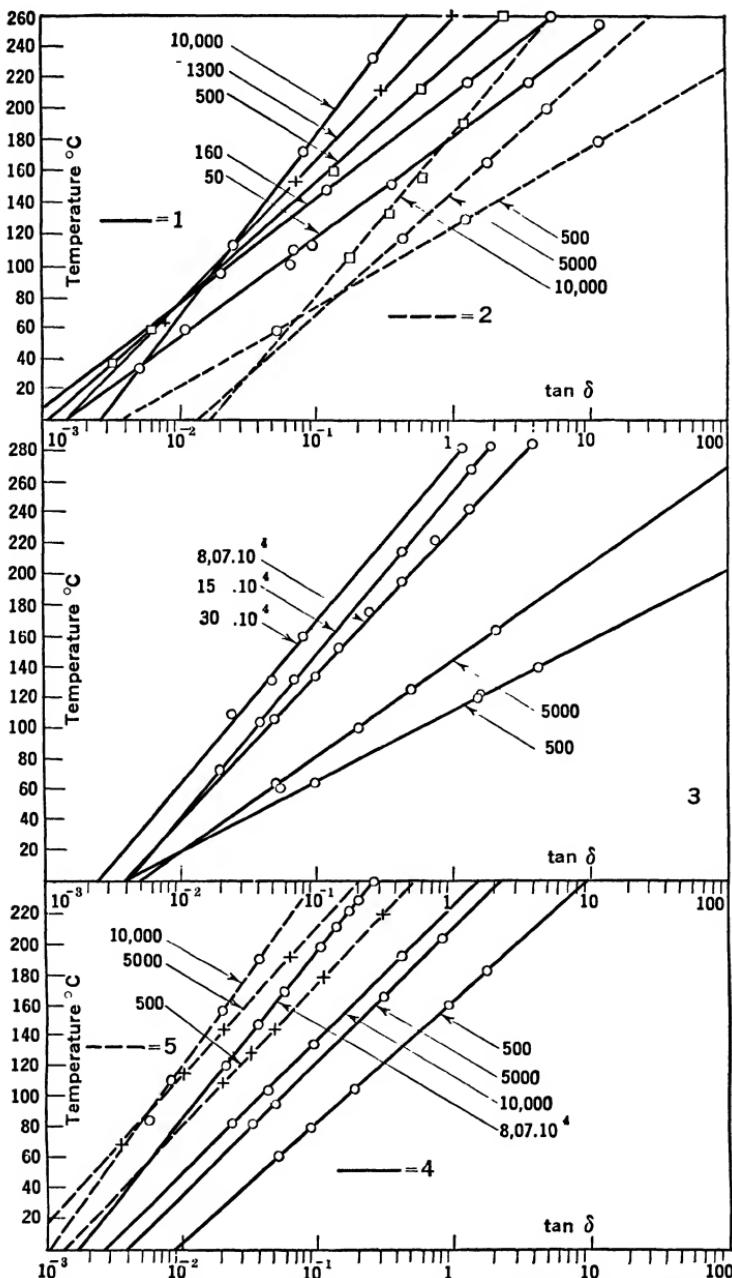


FIG. 46.—Power Factor at Various Frequencies—Temperature. After Strutt.

These values were obtained at a frequency of 500 kc. It is evident that the power loss increases by a factor of approximately 3 for an increase of temperature of 100°C.

6. Relationship of Power Loss to Chemical Composition.—The data on all glasses have been collected in Table 21.

As was stated earlier, a comparison of the power-factor figures of different observers should be made with care. More reliance can be placed on the relative results obtained by any one experimenter.

It was concluded by Schott⁹ that heavy metals such as lead and barium give low power factors and high dielectric constants, and that high alkali content gives high power factor. The compositions of the Schott glasses are not stated with sufficient exactness for comparison of his results with those of others or for independent conclusions as to the quantitative effect of the constituents of the glasses. To say that the alkali is "above" or "below" 10% is far from sufficient. Schott, so far as one can tell from his composition data, used only special glasses and made no measurements on any commercial insulator glasses. High-lead or high-barium glasses as a rule "weather" badly, that is, they are attacked by moisture and are relatively very expensive. He published no data on lime glasses. The glasses studied by Decker⁸ are representative of commercial types, and complete analyses of the glasses are given. The enormous effect of alkali is made very apparent by Decker's data.

McDowell and Begeman also showed qualitatively the effect of alkali in increasing power factor and the effect of lead in decreasing it. They concluded that power factor and the electrical conductivity of glasses at elevated temperatures seem to vary alike, high-resistance glasses having the lowest power factors. This conclusion confirms Schott. However, the McDowell and Begeman glass 6 seems to be quite an exception to this generalization as this glass has much the highest electrical resistivity,

both at low and elevated temperatures, and still has a power factor about three times that of their No. 5 glass. In general, however, power factor follows conductivity, and the conclusions regarding the effect of composition on conductivity may be expected to hold with respect to power factor.

High content of heavy metals in glasses with low alkali content gives high dielectric constant and low power factor. Borosilicate glasses with low alkali content, containing no heavy metals, have both low dielectric constant and low power factor, and hence low power-loss factor. The glass No. 5 in McDowell and Begeman's paper, which is Corning Glass Works glass 707, is the lowest-loss glass reported. This glass has this position because it combines low dielectric constant with low power factor. The low-alkali borosilicate glasses are in addition low-expansion glasses and glasses of high surface stability. In other words, they combine in one material the necessary electrical properties of good insulation and the other essential physical properties of high thermal resistance and chemical stability.

7. Dielectric Absorption, Dielectric Loss, and Power Factor.—Although it is beyond the scope of the present work to present any detailed discussion of the several mathematical theories which have been advanced to explain in terms of absorption and residual charge the dependence of the a-c properties of dielectrics, such as power factor, dielectric loss, and apparent dielectric constant, on the frequency of the applied emf, a few noticeable facts must be brought out in connection with the bearing of such theories on the a-c behavior of glass.

First of all, it is to be noticed that several of the most completely developed and widely accepted theories postulate some form of exponential relaxation function relating the decay of the absorption current with time. In consequence, the several theories, although based on widely different pictures of the underlying mechanism, predict values of the power factor which rise to a maximum and

then decrease again with increasing frequency. This maximum has never been shown to exist in glasses. The fact that the power-factor-frequency curve has never been obtained for any glass over a complete frequency range can perhaps explain why such a maximum has never been noted.

Attention has previously been called to the fact that some measurements on some glasses indicate that power factor is increasing with frequency whereas with other glasses the results are the opposite, that is, power factor is decreasing with frequency. This apparent difference can be explained by stating that the data are on opposite sides of the maximum point on the curve. For the ascending power factors the measurements do not extend to sufficiently high frequencies to attain the maximum; for the descending values the frequencies are beyond the maximum power-factor frequency. This conclusion, however, seems to be scarcely justified, since in the descending values the measurements have been made to as low as 40 cycles per second and no maximum found, and in the ascending-power-factor glasses no maximum was indicated below 500 kc. It would be a very strange fact that in two fairly similar glasses a maximum in one case lay below 40 cycles and in the other case above 500,000 cycles.

From the nature of glass—that is, its conductivity being ionic, its homogeneous structure, its very great viscosity, the very slow rate of decay of its charging current, lasting in some cases for hours—one would conclude that the maximum point on the power-factor curve was at frequencies lower than had been studied. If that be true, the ascending-power-factor measurements referred to are due to some experimental error of the circuit, or to a dielectric heating of the glass increasing the temperature and thus increasing the power factor.

If the power factor of glass is largely determined by an absorption current following some form of exponential law of decay, as seems very possible, then in the same fre-

quency region in which a maximum value of power factor is to be expected there should also be an apparent change in dielectric constant, as can be shown on theoretical grounds. Now Hopkinson found such a change in the "apparent capacity" of a glass condenser at room temperature in the range of very low frequencies. At a frequency of 7.3 the apparent capacity of a glass condenser was found to be approximately twice what it was at a frequency of 100.

Assuming, then, that the increase in capacity observed by Hopkinson is an index of the general frequency region in which to expect a power-factor maximum, the absence of any observed maximum in the literature would be readily accounted for by the fact that in glass at room temperature it would occur at frequencies so small as to be far below the usual range of investigation.

Inasmuch as the physical constitution and properties of glasses can be varied by changes in composition and by heat treatment, it would appear that glass would serve as an ideal material for the study of the fundamental properties of dielectrics.

TABLE 21

Lit.	Glass	Frequency	K	δ	$K\delta \times 10^4$
(1)	198b	6×10^5	11.3	0.00085	96
	102b	6×10^5	7.85	.00041	32
	103a	6×10^5	7.35	.000405	30
	118a	6×10^5	7.35	.000450	33
	318a	6×10^5	7.05	.000545	38
	340d	6×10^5	6.85	.00053	36
	3338a	6×10^5	6.26	.00113	71
	3439a	6×10^5	5.54	.00086	47
	3439b	6×10^5	5.37	.00098	53
	211a	6×10^5	7.41	.000755	56
	3453a	6×10^5	6.55	.0022	140
	3453a	6×10^5	6.64	.00231	150
	3832a	6×10^5	6.94	.002	130
	2188a	6×10^5	6.13	.0034	210
	15a	6×10^5	6.80	.00195	130
	3269b	6×10^5	8.46	.000432	37
	7550a	6×10^5	6.80	.00082	35
	381a	6×10^5	6.90	.00655	450
	5970c	6×10^5	8.07	.00065	52
	2994c	6×10^5	7.90	.000585	46
	1209d	6×10^5	7.80	.000555	43
	211k	6×10^5	7.50	.00078	59
	7185a	6×10^5	5.80	.00179	103
	S336a	6×10^5	7.05	.000505	36
	Quartz	6×10^5000117	
	Fused quartz	6×10^5	3.72	.000117	4.4
	O211	6×10^5000745	
	O211	4.3×10^500072	
	O211	3×10^500071	
	O211	1.87×10^500695	
	O 15	6×10^50019	
	O 15	4.3×10^500183	
	O 15	3×10^500175	
	O 15	1.87×10^500173	
	T163	6×10^500319	
	T163	43×10^500308	
	T163	3×10^500303	
	T163	1.87×10^500298	
	S	550195	
	S	6×10^50051	
	S	4.3×10^500517	

TABLE 21—*Continued*

Lit.	Glass	Frequency	K	δ	$K\delta \times 10^4$
(1)	S	3×10^5	0.00525	
	S	1.87×10^500540	
	0381	1×10^600635	
	0381	6×10^500664	
	0381	4.3×10^500697	
	0381	3×10^500710	
	0381	1.87×10^500755	
	"Lead glass"	550013	
	Do.	1,00000102	
	Do.	2,000000875	
	Do.	"high frequency"00082	
(2)	Pyrex chem. resist. glass	1,000	5	.0082	400
	Do.	1,0000113	(glass strained)
(3)	Do.	5960137	
(3)	Do.	1,0100127	
	Do.	2,9200111	
	Do.	14,00000889	
	Do.	100,00000743	
	Do.	500,00000666	
	Do.	750,000006778	
(4)	Do.	5×10^5	4.9	.0042	200
(5)	Do.	10^3	4.89	.0082	401
	Do.	3×10^4	4.83	.0056	270
(6)	Do.	20	4.88	.0065	316
	Do.	40	4.875	.0055	268
	Do.	80	4.80	.0052	254
(7)	Do.	7.15×10^5	5.8	.0052	
(9)	Do.	7.40×10^5	4.87	.0041	200
	Do.	10^6	5.0	.0038	190
	Do.	1.7×10^7	5.25	.0063	330
(11)	Do.	7.4×10^6	4.8	.0040	192
(10)	Do.	10^300835	
	Do.	3×10^300705	
	Do.	10^400636	
	Do.	3×10^400587	
	Do.	5×10^400577	
	Do.	7.5×10^400569	
	Do.	10^500575	
(3)	No. 1	49800395	
	Do.	1,01500368	

TABLE 21—*Continued*

Lit.	Glass	Frequency	K	δ	$K\delta \times 10^4$
(3)	No. 1	2,820	0.00327	
	Do.	14,00000276	
	Do.	10,00000236	
	Do.	500,00000213	
	Do.	100,00000198	
(3)	No. 2	4980169	
	Do.	1,0150149	
	Do.	3,1300124	
	Do.	1.4×10^400974	
	Do.	10^500766	
	Do.	5×10^50066	
	Do.	10^600617	
(4)	Flint	5×10^5	7	.0042	
	Do.	7.2×10^5	7	.0042	
	Do.	8.9×10^5	7	.00403	
	Plate	5×10^6	6.8	.007	475
(5)	Cobalt	5×10^6	7.3	.007	510
	1	10^3	8.7	.0735	6340
		3×10^4	7.9	.0298	2370
	2	10^3	8.2	.0280	2290
		3×10^4	7.9	.0122	960
	3	10^3	8.0	.0175	1400
		3×10^4	7.8	.0105	820
	4	10^3	8.2	.0245	2000
		3×10^4	7.9	.0175	1380
	5	10^3	8.1	.0228	1845
		3×10^4	7.8	.0122	955
	6	10^3	8.0	.0157	1260
(2)		3×10^4	7.8	.0122	955
	7	10^3	6.8	.0047	319
		3×10^4	6.7	.0035	235
	8	10^3	7.2	.0157	1130
		3×10^4	7.0	.00885	1118
	9	10^3	5.2	.0065	338
		3×10^4	5.1	.00577	295
	11	10^3	4.7	.0049	230
		3×10^3	4.7	.00262	123
	1	10^3	7.5	.0132	990
	3	10^3	6.8	.0031	210
	6	10^3	5.3	.0022	116
	4	10^3	4.7	.0039	183

TABLE 21—*Continued*

Lit.	Glass	Frequency	<i>K</i>	δ	$K\delta \times 10^4$
(2)	5 (Corning 707)	10^3	4.1	0.00077	31
(11)	Corning 707	7.4×10^5	4.4	.00069	30
(9)	Do.	7.4×10^5	4.16	.0006	25
	Do.	10^6	4.16	.0006	25
	Do.	1.7×10^8	4.12	.0017	70
(7)	Do.	7.15×10^5	4.4	.0005	22
(8)	Do.	3×10^4	3.88	.00060	23

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- (8) An industrial research laboratory.
- (9) R.C.A. Radiotron Co.
- (10) Yager and Morgan, *J. Phys. Chem.*, **35**, 2026 (1931).
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CHAPTER V

DIELECTRIC STRENGTH

1. Introduction.—The dielectric strength of a material is the voltage gradient required to puncture the material. This is usually expressed as volts or kilovolts per centimeter or per mil (1 mil = 0.001 in.). In this discussion, kilovolts per centimeter (kv per cm) will be used. Kilovolts per mil will be kilovolts per centimeter times 0.00254.

If the dielectric strength of a material be a physical constant of the material, then it should be independent of the thickness of the material. Under the usual conditions of measurement it has been shown many times that, the greater the thickness of the test specimen, the lower is the measured dielectric strength of the material. The question as to what part of this effect depends upon the material and what part upon the method of test has not been answered, and much additional experimental information on this phase of the problem is required. Comparative tests of different insulating materials, even at the same thickness, very probably lead to erroneous conclusions as to the relative strengths in service, and are valueless unless the tests exactly duplicate operating conditions. Such tests furnish no information as to the actual strengths of the materials, but only as to how the strengths are affected by the particular conditions of the experiment. The problem of measuring the strength of a dielectric in such a manner that the results can be applied to any set of operating conditions is an extremely fascinating one, but so far there is very little fundamental information on solid dielectrics having breakdown strengths comparable to those of glasses.

In this review an attempt is made merely to collect and discuss the existing information on glasses and to summarize the conclusions drawn from the observations cited. Although the data on glasses prove in general that very high potentials are required to produce failure under the test conditions, yet quantitative comparisons of different glasses and other materials should be avoided, unless the test conditions be identical.

If the mechanism of failure were correctly understood, then no doubt there would be certain measurable properties of the material which would determine and evaluate the performance of the body under any set of operating conditions.

2. Early Investigations.—Almy¹ tested a series of five Jena glasses of known composition. The measurements were made on thin plates of glass placed between needle points, with plane and spherical electrodes immersed in oil with an electrostatic machine as a source of potential. He observed that the form and the polarity of his electrodes did not materially affect his results, which are given in Table 22.

He found the relation between thickness and puncture voltage to be given by the formula

$$V_{kv} = \alpha d + \beta \quad (1)$$

where V_{kv} is the breakdown voltage in kilovolts, d is the thickness in centimeters, and α and β are constants.

For glass I

$$\alpha = 126, \quad \beta = 12.45$$

The puncture strength apparently was related in some way to the specific resistance, since, when the glasses were arranged in order of increasing dielectric strength, they were also in order of increasing specific resistance; but resistance changed manyfold while the strength change was only a little more than two to one.

¹ J. E. Almy, Ann. Physik, 1, 508 (1900).

TABLE 22

Glass	Thickness, mm	Puncture Voltage, volts	Strengths, kv per cm	Resistance, ohms per cm ³ at 220° C.
I (709).....	0.41	17,580	429	1.74×10^{10}
	1.42	31,290	220	
	2.28	40,500	177.5	
IV (1722).....	1.49	35,580	238	
	1.60	39,900	249	
V (512).....	0.76	38,250	504	
VI (1675).....	0.41	32,940	775	2.41×10^{13}
XI (1766).....	0.41	41,100	1000	3.7×10^{14}
Crystal quartz perpendicular to axis.....	0.02	22,900	1145	
Crystal quartz parallel to axis.	0.02	30,800	1540	

Almy's tests were made under oil, and for that reason his data meant little. It later developed that it was necessary in dielectric-strength measurements to eliminate the electrode "edge effect."

The importance of the elimination of the edge effect was first shown by Moscicki,² who proved that breakdown strengths of insulation as measured with electrodes immersed in oil to prevent flashover are valueless because the field strengths at the points of failure cannot be computed. The insulation always failed beyond the limits of the electrodes. This suggested to him the possibility of strengthening this zone sufficiently to produce failure under the electrodes. Since his experiments are so fundamentally important, it seems desirable to discuss his work in some detail.

² J. Moscicki, Elektrotech. Z., 25, 527 (1904).

Moscicki studied three glasses, and ebonite, the glasses being (1) ordinary Bohemian alkali glass, (2) alkali-free glass from Schott and Genossen No. 477^{III}, (3) borosilicate thermometer glass, Schott No. 59^{III}. His first experiments were made with 2-mm glass plates under oil with tinfoil electrodes, and he found that all punctures took place beyond the edge of the foil at a voltage of 8 kv. He then experimented with a tube having a 0.3-mm wall with mercury as one electrode, and inside tinfoil on the outside as the other electrode. The tube was left sufficiently long so that the puncture test could be made in air without flashover. Under these conditions the puncture voltage was found to be 24 kv, a value three times that found for the plates used in the oil tests in spite of their much greater thickness. Other tubes with similar electrodes, when tested in oil, failed at 9 kv at the edge of the coating. During the puncture tests in air he observed a corona ring at the edge of the tinfoil, and this he concluded acted as a semi-conducting region to diminish the field intensity and thus to increase the ultimate breakdown voltage. This observation suggested the possibility of protecting the end zones by increased insulation. Strips of mica were wound around these zones underneath the tinfoil edges, so that the mica thickness was gradually increased from the edge outward. The breakdown potential under oil was thus increased from 8 kv to 17 kv, puncture still taking place beyond the edge of the conductor through the mica.

In order to obtain a more gradual transition, a mixture of rosin, beeswax, and vaseline was built up under the edges of the tinfoil, great care being exercised to obtain the correct thickness grading. Other tests were made with the glass tubes having a thin blown section gradually increasing in thickness to the original wall of the tubes, with the addition, in some cases, of the insulating compound.

The results of the tests with and without the dielectric reinforcement are given in the following tables:

DIELECTRIC STRENGTH

TABLE 23
ORDINARY ALKALI GLASS

Wall Thick- ness of Tube, mm, d	Breakdown Potential in Volts, V	Puncture Strength, kv per cm
0.20	6,400	320
0.30	8,750	292
0.40	10,250	256
0.50	11,650	233
0.60	12,750	212
0.70	13,750	195
0.80	14,640	183
0.90	15,460	172
1.00	16,250	162
1.25	17,680	142
1.50	20,400	136
1.75	22,450	128
2.35	24,000	104
2.50	27,000	107
2.70	27,150	100

TABLE 24
ALKALI-FREE GLASS, JENA NO. 477^{III}

Wall Thick- ness of Tube, mm, d	Breakdown Potential in Volts, V	Puncture Strength, kv per cm
0.20	7,000	350
0.30	9,750	325
0.40	12,000	300
0.50	13,480	270
0.60	14,420	230
0.70	15,250	218
0.80	15,980	198
0.90	16,650	185
1.00	17,400	174
1.15	18,300	159
1.24	18,750	151

TABLE 25
BOROSILICATE THERMOMETER GLASS No. 59^{III}

Wall Thickness of Tube, mm, d	Breakdown Potential in Volts, V	Puncture Strength, kv per cm
0.20	7,850	392
0.30	11,200	373
0.40	13,800	345
0.50	15,000	300
0.60	15,800	263
0.70	16,620	236
0.80	17,400	217
0.90	18,200	202
1.00	18,850	188
1.10	19,560	177
1.20	20,340	169

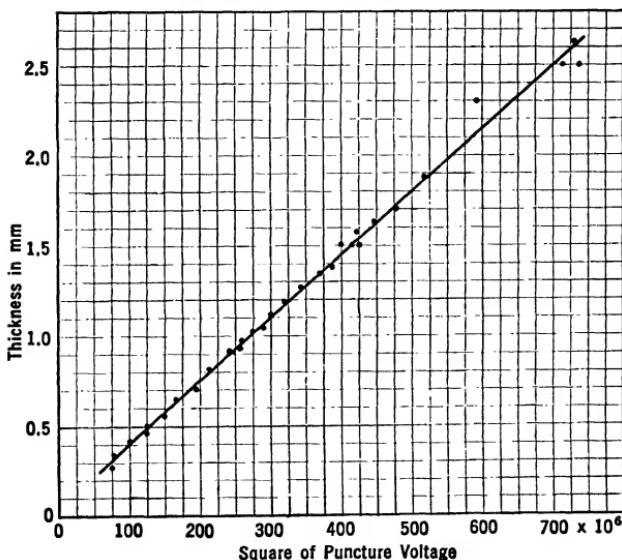


FIG. 47.—Thickness—Square of Puncture Voltage: Edge Discharge Present.
After Moscicki.

Tables 23, 24, and 25 are the results for the tubes without the reinforcement.

The data in Table 23 are shown in the curve, Fig. 47.

This curve shows that over the range investigated the wall thickness divided by the square of the breakdown potential is a constant for any one glass. If this curve be extended to a thickness of 25 mm, or approximately one inch, the indicated puncture voltage is 84 kv. From the authors' experience in measuring the dielectric strength of glasses this value would seem to be much too low. The same kind of extrapolation on glass 3, a borosilicate

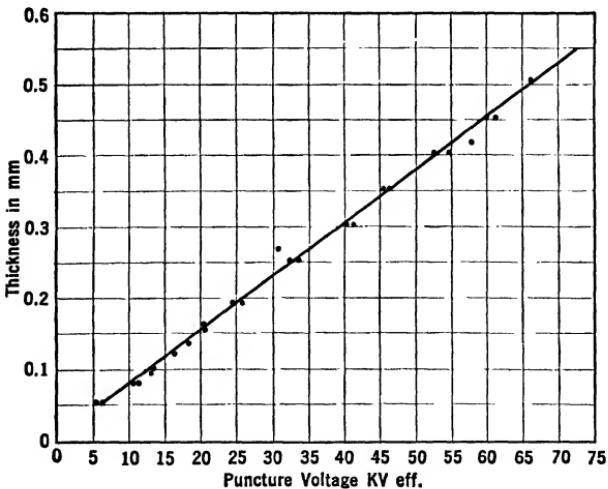


FIG. 48.—Thickness—Puncture Voltage: Edge Discharge Suppressed.
After Moscicki.

thermometer glass, gives a value of 100 kv per in., which again is probably too low.

Table 26 gives the results of the tests on the glass with the dielectric reinforced under the edges of the electrodes. The tests were made in air, and the punctures took place under the coating, which in this case was silver.

The results are shown in the curve in Fig. 48, which indicates a linear relationship between puncture voltage and thickness.

Moscicki² did not apply the voltage gradually, but used a 50-cycle transformer with a resistance in the primary. He adjusted the rheostat, then closed the circuit

TABLE 26
ORDINARY ALKALI GLASS

Wall Thickness of the Thin Spherical Enlargement, mm <i>d</i>	Breakdown Potential in Volts, <i>V</i>	Puncture Strength kv per cm
0.05	6,850	1370
0.05	7,100	1420
0.08	11,050	1381
0.08	11,850	1480
0.09	13,200	1467
0.09	13,800	1481
0.10	13,670	1367
0.10	14,000	1400
0.10	14,450	1445
0.12	16,500	1375
0.13	18,000	1384
0.13	18,560	1427
0.15	20,130	1342
0.15	20,300	1355
0.16	21,000	1312
0.16	20,470	1279
0.18	26,600	1477
0.18	24,700	1372
0.20	27,460	1373
0.20	27,700	1385
0.20	27,500	1375
0.25	33,600	1344
0.25	32,745	1309
0.30	41,055	1368
0.30	40,340	1343
0.35	46,800	1331
0.35	46,053	1315
0.40	54,300	1356
0.40	55,000	1374
0.40	53,500	1338
0.43	58,190	1353
0.45	60,960	1348
0.45	61,404	1364
0.50	67,116	1342
0.55	74,960	1373

only long enough to get a voltage reading. In this way the voltage was increased to the point of failure by a series of increments. Undoubtedly there were many surges when the circuit was closed which his voltmeter did not indicate. The voltages given are the effective volts.

The dielectric strength obtained in this case was approximately 1360 kv per cm or 3460 kv per in. This value which holds up to 0.5-mm thickness is approximately six times that obtained on samples of the same thickness, when the electrode "edge effect" was not eliminated. These tests of Moscicki² show how meaningless are the results of dielectric-strength tests on such insulator materials when the tests are made under oil. His experiments further prove that tests made under oil give no indication of the strength in air. The fact that the strength of his glass (3) under oil was higher than that of the other two glasses may or may not be of some significance. This relatively higher strength might be due to the fact that the test conditions favored this particular glass.

Additional tests made at 8000 to 9000 cycles without eliminating the edge effects gave values considerably below these obtained at 50 cycles, the latter being roughly two and a half times those at the higher frequency. Later work by others indicates that, when mercury electrodes are used, the adhering air film between the electrode and dielectric should be removed under a vacuum. Probably Moscicki's results are somewhat low since he did not observe that precaution. In some cases he used silver-deposited electrodes, which it would seem should give satisfactory results when failure occurred under the electrode. However, work cited later indicates that Moscicki's result of 1340 kv per cm is lower than the true strength. Hence it is concluded that even with silver electrodes the true strength is not necessarily attained.

The necessity for avoiding the electrode edge effect is very apparent. Other investigators, more recently, have

avoided edge breakdown by various schemes. Rochow³ used a biconcave lens of sufficient edge thickness to prevent puncture, and Inge and Walther⁴ immersed their samples in xylol or a mixture of xylol and acetone which eliminated marginal discharges. These measurements are subsequently discussed in more detail.

3. The Effect of the Surrounding Medium.—The measurements of Moscicki² show that the results of the tests are quite different when a preliminary failure of the surrounding dielectric occurs. Littleton and Shaver⁵ cite tests under transformer oil, made on commercial insulators, showing that in dry high-strength oil the insulators failed under voltages about two-thirds of those they had previously withstood in air at 60 lb per sq in. pressure. Insulators tested in transformer oil containing a very slight amount of moisture—just enough to prevent marginal discharge at the voltages of the test—withstood without failure about twice the voltage required to puncture them when in the dry oil. Castor oil having nearly the same dielectric constant as the insulator was also tried, but the results were the same as with transformer oil; that is, the effect of the oil depended on the dielectric strength of the oil and not, so far as could be observed, on the relative dielectric constants of the two insulating media. Of course it is possible that immediately surrounding the electrodes the dielectric constant of the medium at the voltages used might be very greatly different from its low-voltage value.

Inge and Walther⁴ made a comparison of the effect of oils of known properties. Their results on cover glasses 0.075 mm thick are given in Table 27. This glass probably had a dielectric constant of about 7.

The results with a-c and d-c voltages indicate that only the specific resistance of the medium is effective in eliminating preliminary breakdown of the surrounding medium.

³ H. Rochow, Arch. Elektrotech., **14**, 361 (1925).

⁴ L. Inge and A. Walther, Arch. Elektrotech., **19**, 257 (1928).

⁵ J. T. Littleton and W. W. Shaver, Elec. World, **91**, 759 (1928).

TABLE 27

Medium	Dielectric Constant	Specific Resistance	D-c Breakdown Voltage, kv	50-Cycle Breakdown Voltage, kV_{eff}	Impulse Breakdown Voltage, kv
Pentane.....	1.8	7.5×10^{13}	12.8	6.65	7.7
Benzene.....	1.9	5.0×10^{12}	17.4	7.4	7.7
Transformer oil..	2.2	7.4×10^{12}	16.9	7.4	7.9
Castor oil.....	4.4	2.3×10^{11}	18.4	7.4	7.4
Xylol.....	2.35	9.1×10^{10}	18.7	12.8	7.9
Xylol+12% acetone.....	3.1	0.9×10^8	21.3	20.7	9.0

With impulse voltage the properties of the medium appeared to make no difference.

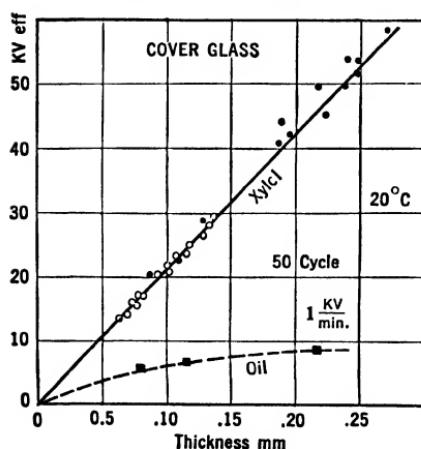


FIG. 49.—Thickness—Puncture Voltage: Tests under Oil and under Xylol. After Inge and Walther.

oil, where the dielectric strength at 0.25 mm is less than 20% of that obtained under xylol.

At a frequency of 4.3×10^5 cycles, Inge and Walther⁶ found that the medium had considerable effect. Their curve is reproduced here as Fig. 50. These tests were made on plates. Tests on blown spheres, eliminating

In order to illustrate further the effect of the medium, the Inge and Walther curve, Fig. 5, is reproduced here as Fig. 49.

When xylol was used as a medium the linear relationship between puncture voltage and thickness was evident, but the results were vastly different from those obtained with transformer

⁶ L. Inge and A. Walther, Arch. Elektrotech., 21, 209 (1928).

marginal discharge, gave approximately the same strength as was obtained for a 0.1-mm plate in xylol.

Inge and Wul⁷ made dielectric-strength measurements under a series of insulating liquids having different dielectric constants. Their tests were made on a sheet of glass 1.4 mm thick, using an impulse voltage having a time interval of 2×10^{-7} second. They used both the direct and reflected wave and symmetrical and non-symmetrical electrodes. Their data are given in Table 28.

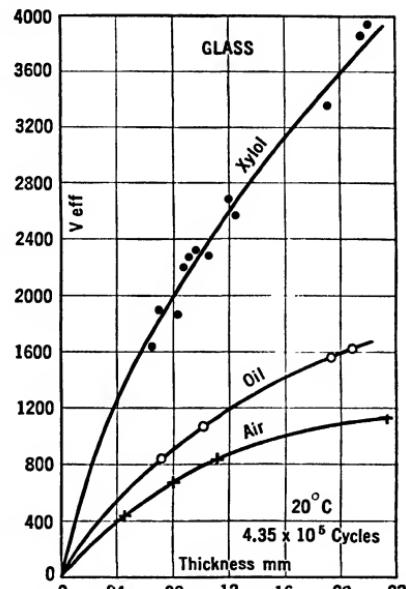


FIG. 50.—Thickness—Puncture Voltage: Influence of Frequency on Surrounding Medium. After Inge and Walther.

TABLE 28

Medium	K	Specific Resistance ρ	Glass							
			Symmetrical Electrode				Unsymmetrical Electrode			
			Reflected Impulse		Single Impulse		Reflected Impulse		Single Impulse	
			V _a	V _d	V _a	V _d	V _a	V _d	V _a	V _d
Hexane.....	1.8	2.1×10^{13}	25	38.5	37	17	37	35.5
Paraffin-oil.....	1.9	1.0×10^{13}	25	39	37	20	38.5	37
Traf-oil.....	2.0	2.0×10^{13}	20	38.5	20	38.5	20	38.5	20	37
Xylol.....	2.3	5.5×10^{11}	33	39	39	39	23	39.5	27.5	35.5
Linseed oil.....	2.7	5.5×10^{10}	41	37	25	41	35.5
Polymerized Linseed oil.....	3.6	2.3×10^{12}	38.5
Aniline.....	7.9	2.2×10^7	36	41	37	25	38.5	35.5
Tricresylphosphate..	8.1	5.5×10^9	65	48.5
Glycerine.....	50.0	2.0×10^6	85

⁷ L. Inge and B. Wul, Arch. Elektrotech., 25, 597 (1931).

The voltage in kilovolts causing breakdown of the insulating medium at the edge of the electrodes was determined photographically and is denoted in the table as V_a . The voltage causing puncture is V_d , K is the dielectric constant, and ρ is the specific resistance of the insulating liquid. These results showed that under impulse voltage tests the minimum or critical voltage causing failure of the glass sample did not depend upon the dielectric constant of the medium, and also was not related to the voltage required to cause a preliminary ~~discharge~~ in the liquid, provided that this voltage was lower than the critical voltage for the glass. When the insulating medium withstood a voltage exceeding the critical, it is probable that the glass sample punctured simultaneously with the breakdown of the medium. When this preliminary discharge was apparently suppressed, the dielectric-strength values of the glass samples were much higher. The authors concluded that failure was not caused by the preliminary discharge alone, and that independent of this discharge, a certain critical voltage characteristic of the insulator material under test must be attained before failure occurs.

Tests with 50-cycle voltages, using the commercial grades of transformer oil and xylol, showed the strength of the glass tested to be approximately 40% greater than when tested under specially purified materials. It is not clear whether the voltages given in the table are the effective or the peak voltage. In either case the dielectric-strength values, even when glycerine was used, are much below those previously obtained by Inge and Walther for 50-cycle and d-c voltages, being roughly only 20% of the former values as shown in Fig. 3.

Additional information on the strength of glass in a non-homogeneous field was obtained by Inge and Walther⁸ where the preliminary breakdown of the surrounding

⁸ L. Inge and A. Walther, Arch. Elektrotech., 24, 88 (1930).

medium was avoided by the method of preparing the test sample. The arrangement is shown in Fig. 51.

The electrode wire a is sealed in the bottom of a glass tube containing mercury for the inner electrode. Consider this a case of a cylindrical conductor parallel to a conducting plane. Let V_s be the field strength at the surface of the wire electrode of radius $2r$ at a distance $d/2$ from the plane electrode, which in this instance is the glass thickness, and V the applied difference in potential. Then the formula for the field strength is

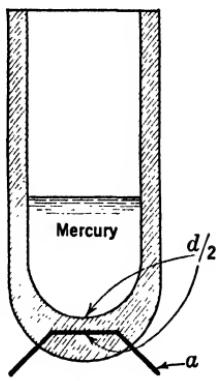


FIG. 51.

$$V_s = 2V(d + 2r)/(r\sqrt{d^2 - 4r^2}).$$

$$\log [(d + \sqrt{d^2 - 4r^2})/(d - \sqrt{d^2 - 4r^2})] \quad (2)$$

In other words, the field strength for a given potential difference, and the degree of uniformity of the field distribution at the surface of the wire electrode, depend upon the diameter of the wire and the thickness of the dielectric at that point. This field strength then can be computed. The data are given in Fig. 52. The puncture voltage of the glass was taken from the curve for homogeneous fields and was used to compute the breakdown voltage for a given size of wire and a measured glass thickness. The curves were drawn from these computations, and it is evident they agree very well with the measurements which are shown as the points on the curves. In the small wires, the measured values were slightly higher than the computed results. In this case the field is concentrated over a thinner layer around the wire, and higher strength values were assumed by the authors. A similar agreement was obtained with d-c and impulse voltage with the exception that when the wire was positive the dielectric-strength values were about 10% higher than when it was negative.

The effect of surface finish was also investigated. The results are as follows:

Polished	3000	kV_{max} per cm
Fine-ground	2360	" " "
Coarse-ground	480	" " "

When the specimens having the differently ground surface finishes were tested under oil instead of xylol the results were all the same. This indicated that the edge failure was not affected by the degree of surface polish.

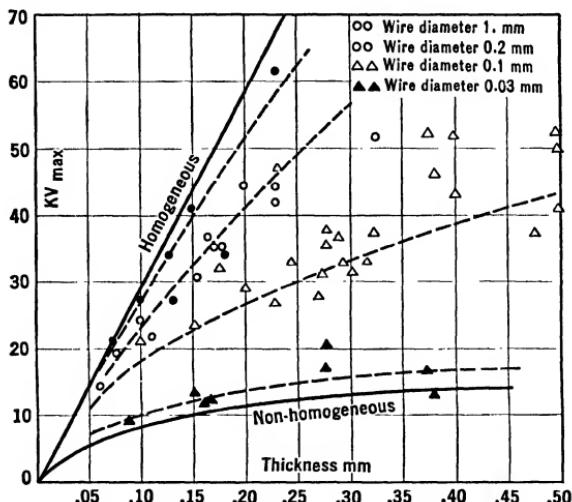


FIG. 52.—Thickness—Puncture Voltage. After Inge and Walther.

- Solid Dots—Wire Diameter 1 mm.
- Circles—Wire Diameter 0.2 mm.
- Open Triangles—Wire Diameter 0.1 mm.
- Solid Triangles—Wire Diameter 0.03 mm.

The action of the preliminary discharges as affecting puncture will be discussed in more detail later.

4. The Effect of the Frequency of the Applied Voltage.—

The relative effects of d-c, low-frequency, high-frequency, and impulse voltages are both of practical importance and of theoretical interest.

For thin sections in uniform fields at room temperature

the puncture strengths under direct, 50-cycle alternating (peak voltage), and impulse potentials are the same when electrodes giving some cooling action are used for the test.

Inge and Walther⁴ made comparative tests on thin spheres tested with both direct and 50-cycle alternating potentials. The results are shown in Fig. 53. It is evident that when the a-c effective volts are changed to maximum volts the strengths for alternating current and direct current are the same.

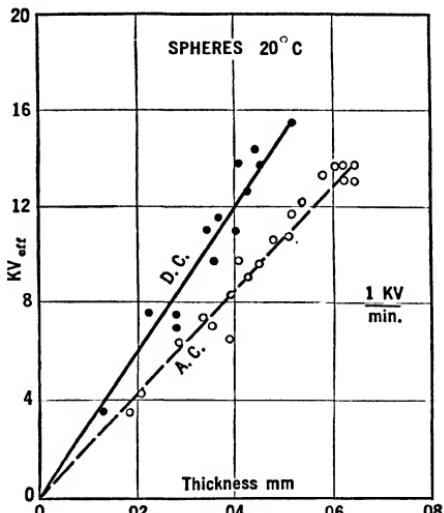


FIG. 53.—Thickness—Puncture Voltage. Direct-Current Voltage Compared to 50 Cycle. After Inge and Walther.

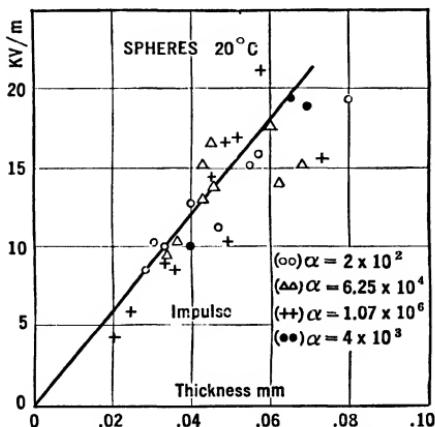


FIG. 54.—Breakdown under Impulse. After Inge and Walther.

The d-c measurements of Moon and Norcross⁹ referred to later were repeated with 60-cycle alternating current by Kenny, Luery, and Moriarty,¹⁰ who found the a-c peak-voltage strengths to be the same as the strengths obtained with the direct current.

The results of tests on the effect of the steepness of the wave front are shown in Fig. 54. The

⁹ P. H. Moon and A. S. Norcross, *J. Franklin Inst.*, **208**, 705-29 (1929).

¹⁰ N. D. Kenny, A. M. Luery, and J. D. Moriarty, *Trans. Am. Inst. Elec. Engrs.*, **51**, 404, 1932.

observations are on blown spheres, thus eliminating edge effects. α is the reciprocal of the time required for the voltage to reach 62% of its final value. There is considerable scattering of the points, but it is apparent that the dielectric-strength values are the same as those shown in Fig. 53.

The dielectric strengths for high-frequency voltages are considerably less than for low-frequency. Inge and Walther⁶ made a number of tests on cover glasses and on blown spheres of Russian apparatus glass. The results are shown in Fig. 49. The effect of the surrounding medium is quite apparent.

A large decrease of strength at 4.35×10^5 cycles, as compared with 50 cycles, is very evident, since the strength obtained on 0.2-mm sample thickness is 180 kv_{eff} per cm

as compared to the figure of 2300 kv_{eff} per cm for 50 cycles, as shown in Fig. 49.

When the tests were made in a vacuum the very low strength of 33 kv per cm was obtained, or only 1.5% of the value for glass immersed in xylol and tested with 50 cycles. Goebeler,¹¹ testing the same "flint" glass that Rochow³ used, obtained a strength of 790 kv_{eff}

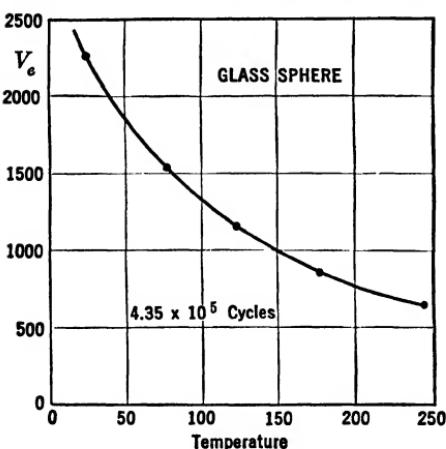


FIG. 55.—Puncture Voltage of Glass Spheres 0.1 mm thick at various temperatures. After Inge and Walther.

per cm at a frequency of 1.12×10^5 cycles as compared with the Rochow value of 2400 kv_{eff} per cm at 50 cycles. However, since this is a fairly high-lead glass, it probably has a low power loss, and hence its loss of strength with frequency

¹¹ E. Goebeler, Arch. Elektrotech., 14, 491 (1925).

would be expected to be less than that of the lime glass studied by Inge and Walther.

Fig. 55 shows the effect of temperature on the dielectric strength when the tests were made with high frequency.

Jost¹² gives the results of measurements on glass plates, probably of lime glass, for frequencies up to 8×10^6 cycles. His voltage values are assumed to be effective volts. His findings are reproduced here as Fig. 56.

The Jost tests were made under transformer oil and hence showed only the effect of the oil for different frequencies. The strength values obtained agree well with values extrapolated from Fig. 50, which were obtained under similar conditions by Inge and Walther.

It is evident that high-frequency tests give considerably lower values of dielectric strength for glass than do low-frequency tests. This is generally ascribed to the internal heating due to the dielectric power absorption, and this fact of decreased dielectric strength is cited as significant evidence favoring the thermoelectric theory of breakdown. However, one can just as well postulate that high frequency does more than heat the dielectric. The rapid periodic elastic displacement of the dielectric particles under high frequency creates more often a configuration favorable to the breakdown of the dielectric which results in lower dielectric strength. Besides, the high-frequency alternations might well have some increased ionization effect apart from the increased thermal agitation.

In addition to the question of the effect of frequency and wave form for rapidly increasing voltages, there is the

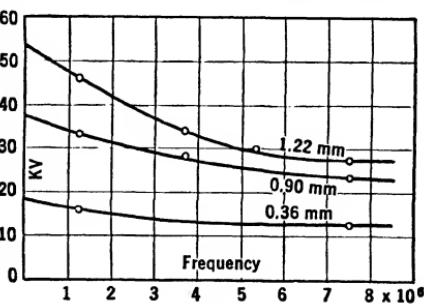


FIG. 56.—Puncture Voltage—Frequency.
Glass in Transformer Oil. After Jost.

¹² R. Jost, Arch. Elektrotech., 23, 305 (1929).

problem of the fatigue action due to continuously applied and intermittent loads. Contrasted with the fatigue effect there is the question of the effect of aging. These two should not be confused; fatigue may be defined as the gradual weakening under stress with a return to normal when the stress is removed; aging is a permanent weakening of the material.

The effect of the duration of the load was studied by Inge and Walther¹³ and is shown in Fig. 57. The curves show that a weakening under load appeared after 3 seconds. After 1000 seconds the strength is about 50% of the

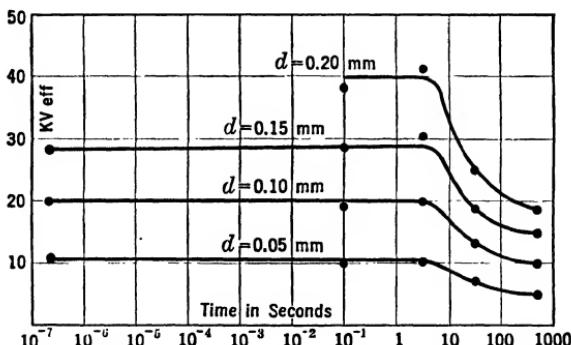


FIG. 57.—Effect of Time of Load, Uniform Field. After Inge and Walther.

initial strength and appears to have attained a constant value. However, the degree of weakening must be largely determined by the balance between ratio of development and dissipation of heat, if this decrease in strength be a thermal effect. In other words, the amount of fatigue may depend on the particular conditions of the experiment rather than be a property characteristic of the material.

In no instance is there any evidence of an effect traceable to an aging of the glass. The evidence, though indirect, leads to the conclusion that no such effect exists. In the case of direct currents at elevated temperatures such an effect is to be expected, owing entirely to the

¹³ L. Inge and A. Walther, Arch. Elektrotech., 22, 410 (1929).

electrolysis and the attendant change in the composition of the glass. Data bearing on this question were obtained by Jost,¹² who tested glass under successive impulses, and his conclusion was that if the specimen would stand as many as twenty impulses, it would stand an indefinite number. Jost, however, made all his tests under some insulating medium where electrode edge effects were present, and for that reason his results are difficult to interpret.

5. The Variation of Dielectric Strength with Temperature.—The effect of temperature on the dielectric strength of glass is of considerable importance from both the practical and theoretical points of view. The Wagner¹⁴ theory of dielectric failure is based on the fact that dielectrics such as glass become more conducting as their temperature increases. Wagner presupposes current flow and ohmic heating of the dielectrics, which become locally concentrated in a narrow zone or canal of initially slightly higher conductivity than that of the surrounding material. This conduction current heats the dielectric along this canal, which results in a decrease in resistance and in turn in a further increase in current. If the voltage be sufficiently high this process ultimately leads to failure. Rogowski¹⁵ determined the voltage-current characteristics of dielectrics, assuming uniform conductivity of the material and not the canal structure of Wagner. He found the heating theory insufficient to account for the facts observed during impulse failure and the failure of thin dielectrics; but at the same time no purely electrical theory of failure was sufficient to explain the behavior of thicker materials under a continuous electrical stress. Accordingly he developed a thermoelectric theory from considerations of both the thermal effect and the purely electrical effect.

Rogowski's theory assumes a maximum field strength in the material which cannot be exceeded without failure, and yet a dielectric in which heating caused by the con-

¹⁴ K. W. Wagner, Am. Inst. Elec. Engrs., **41**, 288-299 (1922).

¹⁵ W. Rogowski, Arch. Elektrotech., **13**, 153 (1924).

duction current is taking place. For short time intervals, and in thin plates having the surfaces cooled, the internal heating is small and failure will be largely due to the purely electric effect; but where the thickness is large and heating is appreciable then thermal effects operate to produce the breakdown. According to Poole,¹⁶ the resistance of the dielectric and hence also the conduction current is a function of the field strength. This relation is expressed by:

$$R = R_0 e^{-\gamma\theta} e^{-V/V_0} \quad (3)$$

where θ is temperature, R_0 and R specific resistances, V and V_0 field strengths, and γ a constant. Since this equation does not show any sudden change in R at voltages just below puncture, Rogowski modified it as follows:

$$R = R_0(1 - V/V_0)e^{-\gamma\theta} \quad (4)$$

so that

$$R = 0 \quad \text{for } V = V_0$$

On the basis of this equation, Rogowski developed the relationship between current and applied voltage for different assumed boundary conditions, so that his theory may be tested experimentally.

These two theories of thermal action and the purely electrical theory have furnished the basis for the greater part of the studies of the effect of temperature on the dielectric strength of glasses.

Rochow,³ using 50-cycle alternating current, found a constant strength for temperatures between -18° and $+90^\circ$ C. He eliminated edge effects as his glass samples were biconcave lenses tested under xylol. He removed by evacuation all adhering gas bubbles from the mercury electrodes. He found that puncture usually occurred at the center of the electrodes, showing that edge effects were eliminated by this treatment. The glass tested was Jena flint glass 0118, having a refractive index of 1.6129 for the

¹⁶ H. H. Poole, Phil. Mag. 42, 488 (1921).

sodium D lines, a specific gravity of 3.58, and a dielectric constant of 7.4. His results for dielectric strength are given in the curve, Fig. 58. These results should be compared with those of Mündel,¹⁷ whose measurements were made in a vacuum to prevent edge discharge. The data by Mündel on 0.4-mm plates of a glass having the composition SiO_2 70.6%, Na_2O 16.8%, K_2O 1.1%, MgO 3.5%,

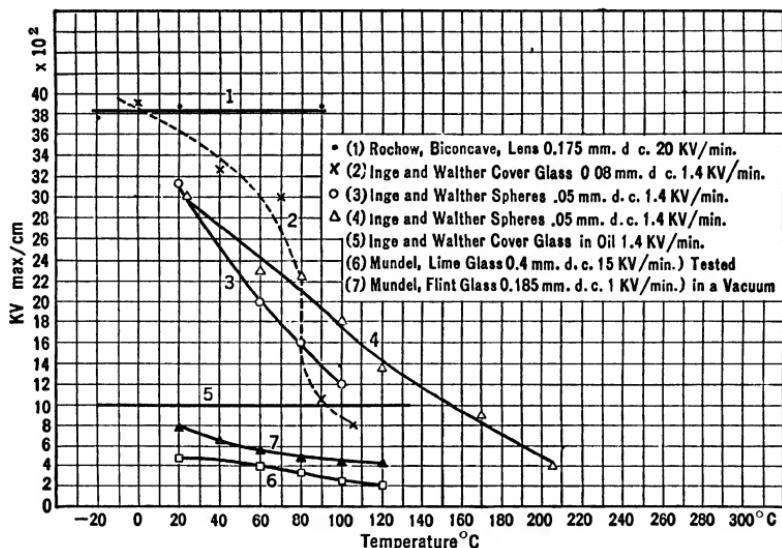


FIG. 58.—Variation of Puncture Strength with Temperature.

- ... (1) Rochow. Biconcave Lens 0.175 mm. D-c. 20 kv per min.
- xxx (2) Inge and Walther. Cover Glass 0.08 mm. D-c. 1.4 kv per min.
- ooo (3) Inge and Walther. Spheres 0.05 mm. D-c. 1.4 kv per min.
- (4) Inge and Walther. Spheres 0.05 mm. D-c. 1.4 kv per min.
- (5) Inge and Walther. Cover Glass in Oil. 1.4 kv per min.
- (6) Mündel. Lime Glass 0.4 mm. D-c. 15 kv per min. Tested in the vacuum.
- (7) Mündel. Flint Glass 0.185 mm. D-c. 1 kv per min.

CaO 5.5%, BaO 2%, R_2O_3 0.5% are given in curve 6, Fig. 12. This is a soda-lime glass with a high temperature coefficient of electrical resistivity, due to its high alkali content. Curve 7 by Mündel shows data on a "flint" glass which is probably quite similar to the glass used by Rochow. It is apparent that this glass gave somewhat

¹⁷ E. Mündel, Arch. Elektrotech., 15, 320 (1925).

higher strengths than that in curve 6, but was still far from being equal in strength to the glass of Rochow. This cannot be caused by the slower voltage application rate of Mündel, the rate of Mündel being 1 kv per min as compared to 20 kv per min for Rochow, since Mündel's own tests showed that a change in rate of voltage application from 15 kv per min to 0.04 kv per min only changed the strength at 20° C from 430 kv per cm to 395 kv per cm. At 110° C the ratio of the dielectric strength values obtained at the two extreme rates of voltage increase was about 2 : 1. This definitely leads to the conclusion that in the vacuum of Mündel the heat loss from the insulator test piece was very small, as it was largely surrounded by a metallic reflecting electrode which reduced radiation loss and the vacuum eliminated conduction and convection losses. This conclusion is confirmed by the experiments of Inge and Walther,⁶ who obtained a strength in vacuum of only one-seventh of that obtained when the specimen was tested under xylol. These particular tests were made with high-frequency currents, which might tend to accentuate the difference on account of the greater amount of internal heating.

Under the conditions of his tests, Rochow had almost no dielectric heating. A test for localized heating was made by means of a device to inspect for optical homogeneity, which was sensitive enough to detect a localized 10° C rise in temperature in the specimen during test, yet no such rise was observed. The specific resistance of Rochow's glass changed by a factor of 4×10^5 in the temperature range of the experiments, yet there was no change in dielectric strength. According to the theory of Rogowski, puncture voltage should have changed by a factor of 630.

The mercury electrodes of Rochow controlled the increase in temperature of the glass. The measurements of Mündel accordingly do not represent the strength of the glass at the temperature stated, but only that of the glass at the unknown temperature just preceding puncture.

Curves 2, 3, and 4, Fig. 58, are taken from Inge and Walther,⁴ curve 2 showing the results on cover glasses immersed in xylol as the insulating liquid, and curves 3 and 4 the results on thin hollow spheres having mercury electrodes. In all cases the surfaces of the test pieces

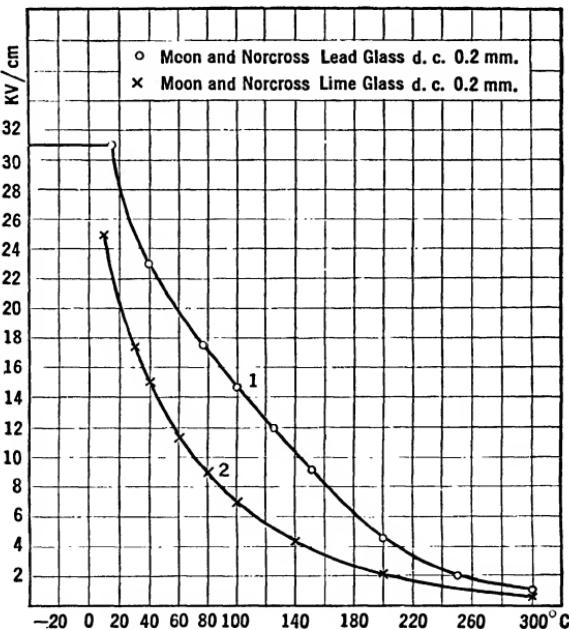


FIG. 59.—Dielectric Strength—Temperature, D-c Voltage. After Moon and Norcross.

- (1) Lead Glass 0.2 mm thick.
- (2) Lime Glass 0.2 mm thick.

were maintained reasonably near the temperatures measured.

Curves 1 and 2, Fig. 59, show data obtained by Moon and Norcross⁹ on a lime glass and a lead glass. Curve 2 was obtained with plates immersed in insulating liquids and curve 1 with thin spheres. In both cases, rise of temperature of the glass was retarded by the cooling of the medium and the electrodes. The authors state that the rate of voltage increase was uniform and adjusted so

that the time of application preceding puncture was about ten minutes. Their preliminary tests proved this factor to have no effect on the puncture voltage.

Fig. 60 is from Moon and Norcross on "lead glass."

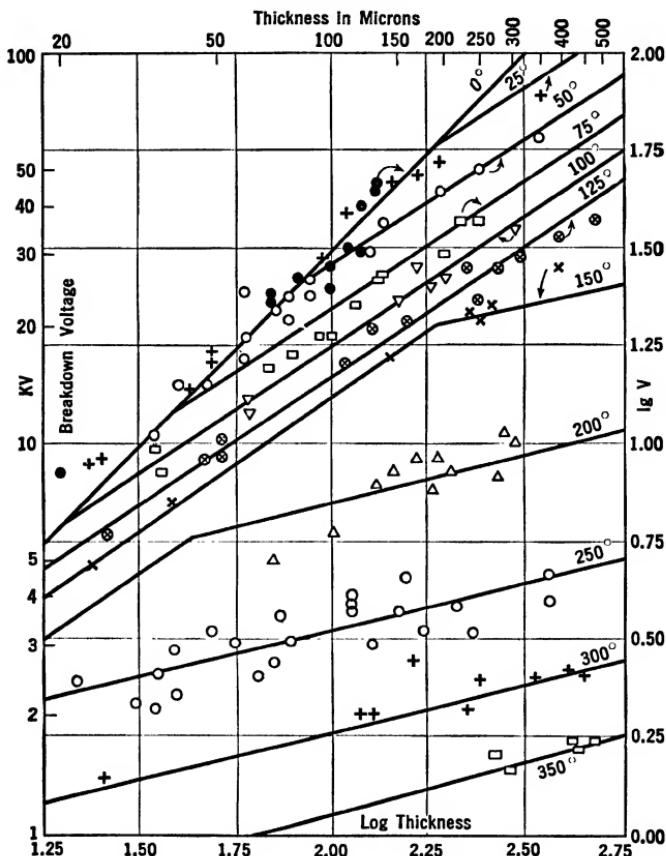


FIG. 60.—Thickness—Puncture Voltage at Various Temperatures.
After Moon and Norcross.

The data so plotted indicate three regions of breakdown which are designated as "disruptive," "intermediate," and "thermal," according to the supposed type of breakdown. However, these three regions of breakdown are apparently not so well defined as the straight lines in the

graphs would indicate. Their data are reproduced in our Fig. 61 with curves redrawn so as to pass more nearly through the mean positions of the points. They deviate considerably from the position of the original curves, so

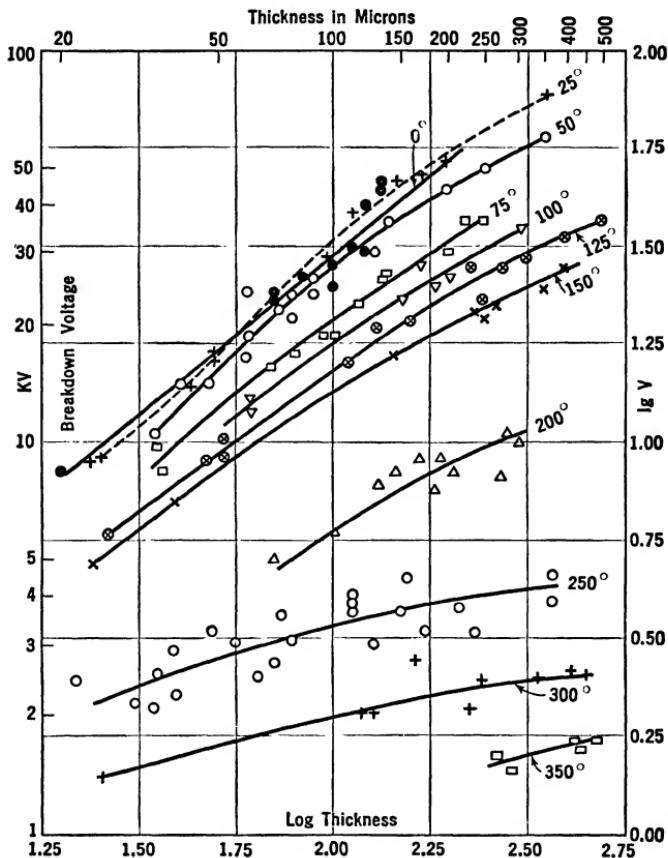


FIG. 61.—Thickness—Puncture Voltage at Various Temperatures.
Redrawn from Data by Moon and Norcross.

that the straight-line characteristics are no longer evident. The relation between $\log V$ and $1/T$ is shown by the dotted curves in Fig. 62 with the original curves of Moon and Norcross reproduced for comparison. It is evident that there are a disruptive region, a thermal region, and

DIELECTRIC STRENGTH

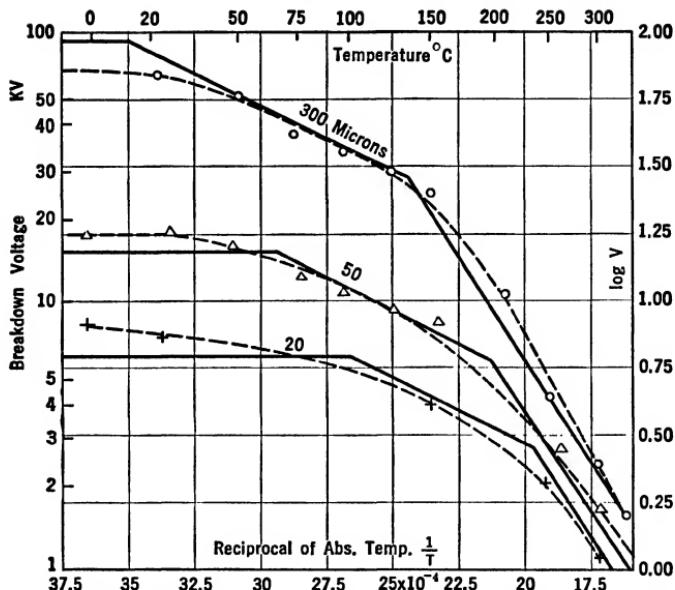


FIG. 62.—Puncture Strength—Temperature. After Moon and Norcross.



FIG. 63.—Log Puncture Voltage—Reciprocal of Absolute Temperature. After Inge and Walther.

(1) Specific Resistance at 200° C = 2.08×10^7 .
 (2) Specific Resistance at 200° C = 4.06×10^6 .

a region for the transfer from one to the other, but there is no definite boundary demarcation between these zones. This conclusion is in agreement with that of Inge and Walther. Kenny, Luery, and Moriarty,¹⁰ following the same experimental procedure as Moon and Norcross except for using 60 cycles instead of direct current, state that the observations were not sufficiently accurate to determine whether the transitions should be denoted by sharp discontinuities or by gradual transitions.

There seems to be some relationship between the specific resistance of a glass at high temperatures and its break down voltage. Inge and Walther¹⁸ have investigated this factor, and their results for two glasses are shown in Fig. 63. The glass with the higher resistance has the higher dielectric strength. The tests below 200° C were made under oil.

Fig. 64 shows the relation between change of strength and the change of resistance with temperature. Also the log of resistance changes with $1/T$ just twice as rapidly as does the log of puncture voltage, which agrees quantitatively with the theory of Rogowski.

The general conclusion from these measurements on thin glass plates is that the Rogowski thermoelectric theory serves as an interpretation of the observed facts but that it cannot be quantitatively verified, owing to the lack of

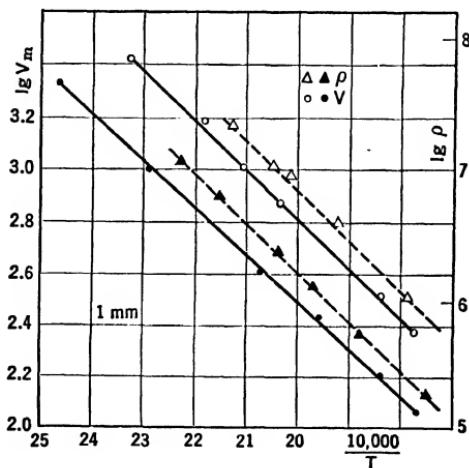


FIG. 64.—Log Puncture Voltage—Log Specific Resistance—Reciprocal of Absolute Temperature. Same glasses as in Fig. 63. After Inge and Walther.

¹⁸ L. Inge and A. Walther, *Z. Physik*, **37**, 292 (1926).

information as to the temperature of the specimens and the exact current and field distribution in the specimen under test. Any factor that increases the temperature of the dielectric, such as long-continued application of voltage, tests under thermally insulated conditions, and the application of high frequencies producing heating by dielectric loss, should decrease puncture strength by an amount depending upon the change in temperature. The data cited seem to indicate this to be a fact.

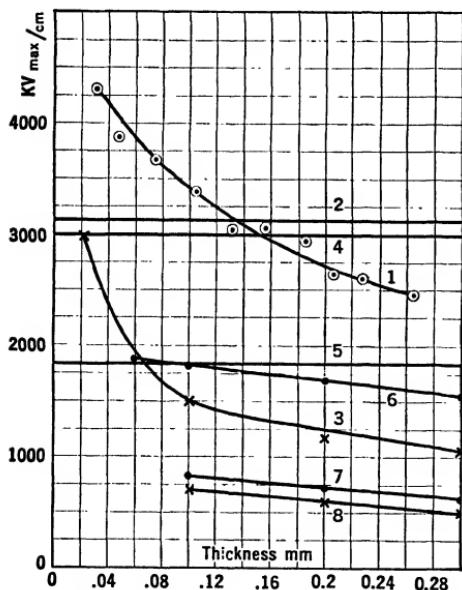


FIG. 65.—Variation of Dielectric Strength with Thickness.

- (1) Data by Rochow.³ Flint Glass.
- (2) Data by Moon and Norcross.⁹ Lead Glass, 20° C.
- (3) Data by Moon and Norcross.⁹ Lime Glass, 20° C.
- (4) Data by Inge and Walther. Cover Glasses and Russian Apparatus Glass.
- (5) Data by Moscicki.²
- (6) Data by Güllner.²¹
- (7) Data by Mündel.¹⁷ Flint Glass.
- (8) Data by Mündel.¹⁷ Lime Glass.

$P_v = a\sqrt{d}$ for cases where there was edge effect or non-homogeneous fields, and $P_v = ad$ for homogeneous fields. He tested only thicknesses of about 2 mm or less, and his results were for 50 cycles, alternating current. The results of Almy for direct current have been given.

6. Variation of Dielectric Strength with Thickness.—In general, dielectric strength is supposed to decrease with increasing thickness according to some function of the thickness. On account of the very high dielectric strength of glass, only comparatively thin thicknesses have been studied. As was mentioned earlier, Moscicki² found that

The data of different observers have been collected and are shown in Fig. 65. Electrode edge effect is presumed to be eliminated in all these tests.

It is very apparent that the different observers obtain widely different strengths, with no agreement as to a constancy of strength with thickness even in the very thin specimens tested. Inge and Walther found the same strengths for impulse, direct current, and the peak voltage of 50-cycle alternating current.

Data on very thin sheets of glass are given by Joffé,

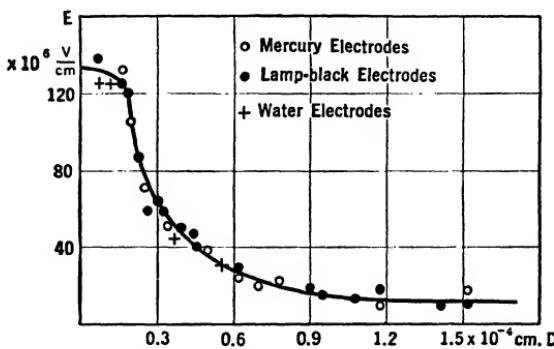


FIG. 66.—Thickness—Dielectric Strength. After Joffé, Kurchatoff, and Sinelikoff.

Kurchatoff, and K. Sinelikoff.¹⁹ Their data are shown in Fig. 66.

7. Relationship between the Dielectric Strength and the Composition of Glass.—The previous discussions have shown the futility of attempting to draw any conclusions concerning the question of the effect of composition on the dielectric strength of glasses. Moon and Norcross²⁰ concluded that the dielectric strength in the disruptive region is proportional to the silica content of the glasses. Of course, tests on four different glasses of such widely dif-

¹⁹ A. Joffé, T. Kurchatoff, and K. Sinelikoff, *J. Math. Phys.*, Mass. Inst. Tech., April, 1927, 133-144.

²⁰ P. H. Moon and A. S. Norcross, *Trans. Am. Inst. Elec. Engrs.*, **49**, 755 (1930).

ferent composition as were tested by them, all containing four or more components, in various proportions, could furnish no information as to the effect of the separate components. As a matter of fact, the dielectric strengths obtained by them in the disruptive region are inversely proportional to the probable dielectric constants of their glasses, which might be of some significance, but they are also inversely proportional to their specific gravities and indices of refraction, which probably is of no significance.

In the temperature zones where thermal failure occurs it will very probably be found that the compositions giving the highest electrical resistivities at those temperatures will give the greatest resistance to puncture, and hence the conclusions cited for the effect of composition on specific resistance will apply to dielectric strength. For high-frequency voltages the compositions showing the lowest power factors can be expected to furnish the greatest resistance to failure. There is practically nothing in the literature to indicate what might be the most desirable composition to withstand impulse voltage or high voltages in the low-temperature zone where disruptive or electrical failure occurs.

8. The Nature of Dielectric Failure in Glass.—It has been pointed out that the dielectric strength of glass is affected by the temperature in a peculiar manner, the glass becoming progressively weaker with increasing temperature after a critical temperature is exceeded, whereas below the critical temperature the glass strength remains constant even though the specific resistance changes tremendously. The dielectric strength of glass seems to be a real physical constant of the material when tests are made at ordinary temperature on thin sections. It is argued by some that the strength of thicker sections becomes less as the sections increase in thickness on account of internal heating and the inability, due to the poor thermal conductivity of the glass, to dissipate this internal heat. High-frequency currents heat the glass by reason of dielec-

tric losses and are thus supposed to cause a lowering of strength by increasing the temperature. On the other hand, there seems to be little indication of a relationship between the specific resistances of glasses or their power factors and the dielectric strength at room temperature. The data in this respect conflict. The original tests of Almy¹ showed no definite connection between the specific resistance and dielectric strength of the glass. However, electrode edge effect was present in Almy's tests, and hence his results are of little absolute value. GÜllner²¹ tested eleven glasses which varied in resistance by a factor of 2000 while the dielectric strength values varied only by a factor of 2. Hence it can be stated that the initial resistance of the glass apparently has little effect on the dielectric strength of the glass. Yet Inge and Walther found, as is illustrated by Figs. 63 and 64, a parallel effect between breakdown voltage and specific resistance. The slope of the $\log \rho - 1/T$ curve is just about twice that of $\log V/m - 1/T$ curve, which is in accord with the Rogowski development. Rochow found puncture strength to remain constant in the same temperature interval that caused a change in the specific resistance by a factor of 4×10^5 .

The decrease of strength with increasing frequency of the applied voltage may be a heating effect, or it may be due to the electrical effect of the higher frequencies. So far as one can estimate from the observations, the puncture strength at a frequency of 4.35×10^5 is about the same as that of the glass at a temperature of 200° C when tested with 50-cycle alternating current.

The failure under impulse voltage is considered to be a purely electrical phenomenon. The exact nature of this type of failure has been the subject of considerable discussion. There are two theories, one of ionization by impact, and the other of an ionization of the atoms by means of the intense fields. Apparently the theoretical voltage required

²¹ G. GÜllner, Arch. Elektrotech., 21, 267 (1928).

to tear electrons from the atoms is greater than experiment indicates to be the dielectric strength of the material, and hence the latter theory seems to have little experimental justification. The ionization-by-impact theory is more in accord with the facts.

A study of the failures due to marginal discharges and progressive failure of the material should give some positive information on the nature of electrical puncture. These studies favor the ionization-by-impact theory of failure. Partial punctures in glass seem to have been first observed by Du Moncel,²² who noted the spark from the negative pole of an induction coil intermittently breaking its way through the glass test piece. Quincke²³ observed a discharge from the positive pole of an induction machine which he stated would at times partially puncture the glass before complete penetration occurred. He made a number of observations on the form of the puncture paths and concluded that the discharge was driving gas into the glass. The cracks and strains in the test piece, to which he ascribed considerable importance, however, have the appearance of being of a purely thermal origin, being caused by the contraction of the glass after having been melted by the current following the puncture.

J. T. Littleton and W. W. Shaver²⁴ give photomicrographs of partial punctures observed in tests with 60-cycle alternating current on glass insulators. Such results are usually obtained when the insulator is tested in oil of high dielectric strength. However, they have been observed occasionally in tests in air where the field is locally distorted by some surface defect such as a crack. Fig. 67 is a photograph of such a puncture. The discharge started from the bottom of a crack in the pinhole cavity and advanced towards the tie wire groove. Several minutes were required to give the degree of advancement shown.

²² Du Moncel, *Fortschr. Physik*, **14**, 488 (1858).

²³ G. Quincke, *Ann. Physik*, **48**, 113-144 (1915).

²⁴ J. T. Littleton and W. W. Shaver, *Elec. World*, Sept. 10, 1927.

The appearance of this partial puncture is identical with that of those obtained under oil.

L. Inge and A. Walther²⁵ show a number of photographs of such partial punctures caused by impulse discharges with the dielectric and electrodes immersed in oil. Even when the glass plate was completely punctured on the first impulse test the second impulse discharge did not follow

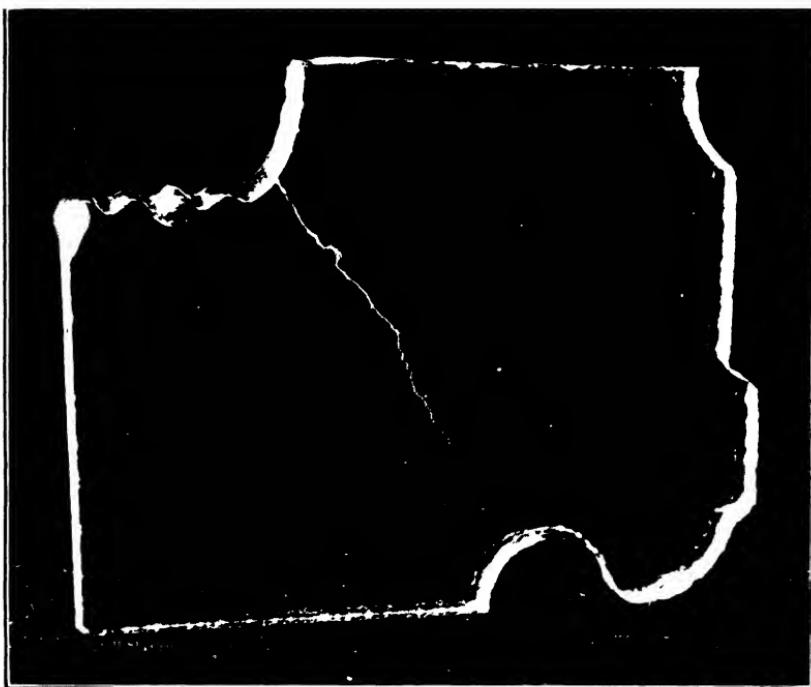


FIG. 67.—Photograph of Path of a Partial Puncture.

the path of the first, and the puncturing process could be repeated many times. Littleton and Shaver called attention to the close similarity of the appearance of the partial puncture to that of natural lightning. As partial-puncture paths are studied in close detail this similarity becomes still more striking.

Inge and Walther concluded that such punctures were

²⁵ L. Inge and K. Walther, Arch. Elektrotech., **24**, 259 (1930).

caused by impact ionization, and that at the surface of the dielectric the field strength at the instant of impact of the discharge is several thousand kilovolts per centimeter and in the case of thin films (0.01 mm) even as high as 10,000 kv per cm.

Electrode edge discharge is assumed to cause failure at the same field strength as has been observed for thin sheets in homogeneous fields for short-time loading, and to be the same as existed in the case of impulse voltage causing puncture. This field strength apparently exists for such a short interval of time that puncture is not completed. The selection of the point of impact of the discharge starting penetration is no doubt controlled by surface irregularities tending to locally increase the field intensity at this point. Such points therefore are in effect points of weakness even though the material may not actually be any weaker at these points. If there could be some way of determining these actual field strengths, the true dielectric strength of the material could probably be very accurately measured by this method. The mechanical strength of glass has been measured in such a manner by Griffith,²⁶ who obtained mechanical strengths of glass as high as 340,000 lb per sq in. (240 kg per sq mm) by correcting for the surface imperfections. This strength is about thirty times that usually obtained on glass samples where the intensification of stress around surface irregularities is neglected.

The impact of the discharge through the oil suddenly overstrains the surface layer and failure starts. The energy released may not be sufficient to cause complete penetration of the material. If the voltage be maintained, a second discharge rapidly follows in the presensitized path which may penetrate further, or the energy may be absorbed by the oil and the path in the dielectric without making any noticeable progress. In this manner, partial puncture discharges occur which fail to make further

²⁶ A. A. Griffith, *Trans. Roy. Soc. London*, **221**, 163 (1920).

progress after the first few seconds of the test. Inge and Walther observed that puncture took place at a constant voltage independent of the voltage causing the pre-breakdown of the oil. This does not agree with the observations of the authors of this book, who have frequently observed during tests on commercial insulators that any discharge through the oil which can be maintained would eventually puncture the insulator at some point. The voltage required to maintain the discharge depended upon the initial moisture content of the oil; the drier the oil, the lower the voltage necessary to cause the discharge, and hence the lower the ultimate puncture voltage of the insulator.

Meyer²⁷ assumed that the electrical strength of the dielectric depended on the temperature; being lessened by an increase in temperature. He then arrived at an explanation of puncture as being dependent on temperature, quite apart from the growth of any conduction current. Meyer's theory is therefore quite different from the Wagner thermal theory, which assumed a thermal breakdown caused by the electrical field.

No theory seems to be in entire agreement with all the observed facts. This might possibly be due to the observations not being entirely reliable, or rather, not including all the possible factors. Although attention has been directed to the great effect of electrode edge discharges on the dielectric-strength tests, and the assumption is tacitly made that the experiments in which edge discharges were eliminated give the true dielectric strength of glass, there is little positive proof that this is the case. It has been shown that many properties of glass, such as the electrical resistivity, power factor, and specific gravity, depend upon its past thermal treatment, yet all the experiments cited fail to consider this factor as affecting dielectric strength. The blown glass spheres probably were unannealed and the

²⁷ K. Meyer, Arch. Elektrotech., 24, 151 (1930).

cover plates and biconcave lenses annealed. Glasses are also known to contain large amounts of dissolved gases, often as much as 100% by volume, which may have considerable effect on their dielectric strength.

It is probable that all the measurements have been complicated by the large effects of some of these unconsidered experimental variables, and that the true strength of glass is still considerably higher than the present results indicate it to be. As measured it is purely a point effect, depending upon the field strength at that point and the velocity and energy of the bombarding ions. It appears that research directed towards measurement of these other factors would be profitable. So far the attempts have been directed towards their elimination, but there is considerable doubt as to how completely this elimination has been accomplished.

9. The Dielectric Strength of Thick Sections of Glass.—All the work discussed so far has been on thin sections of glass. The majority of the measurements reported were made on sections not exceeding 0.25 mm in thickness. The reason for this is fairly obvious, since attempts were made to avoid electrode edge discharges, and this problem becomes almost insurmountable at the higher voltages required to puncture greater thicknesses. Thick sections, that is several centimeters thick, are readily punctured under oil, but that gives no information as to the strength in air, which in the majority of cases is the only condition of practical importance. One can perhaps safely conclude that if a section only 0.2 mm thick requires a voltage of 60 kv to cause puncture then a section a centimeter or more thick is perfectly safe to use at this voltage so far as puncture is concerned. However, if the voltage gradient in service is such that a pronounced corona is formed, then the question as to the effect of the action of this corona has to be answered. So far this problem seems to have been completely neglected.

It seems worth while, however, to review the small

amount of available information on measurements made on thicker sections of glass.

Moscicki² tested under oil a soda-lime glass 2.7 mm thick and obtained a strength of 142 kv_{max} per cm. Under these conditions of test he found that the square

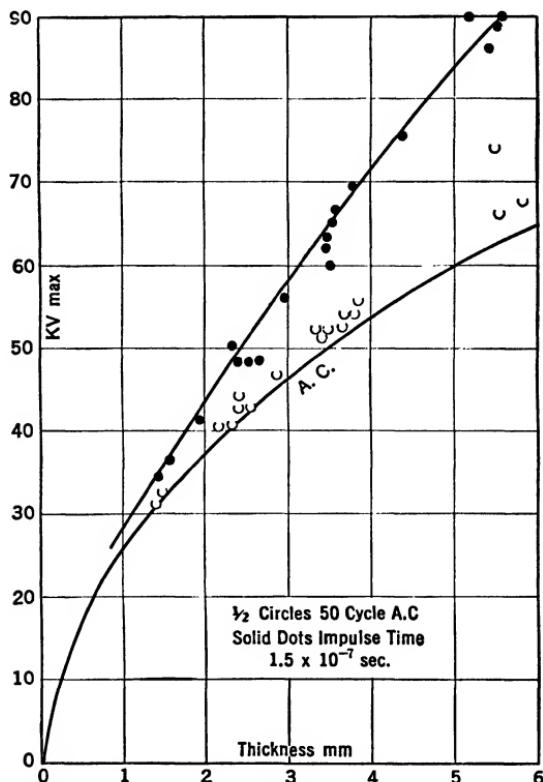


FIG. 68.—Puncture Voltage—Thickness. After Inge and Walther.

Semicircles, 50 cycle a.c.
Solid dots, Impulse time 1.5×10^{-7} sec.

of the puncture voltage was proportional to the thickness. If his results be extrapolated the strength at one centimeter is 74 kv_{max} per cm, and at 1 in. 118 kv_{max} per in.

Inge and Walther²⁵ gave the results of measurements on plate glass tested under oil between 25-mm-diameter

plane disc electrodes with rounded edges. Their measurements were made with impulses of different duration and with 50-cycle alternating current. Their curve for an impulse time of 1.5×10^{-7} second and for 50 cycles is reproduced in Fig. 68.

The same relation between thickness and the square of puncture voltage observed by Moscicki holds approximately for the 50-cycle curve for the interval 2 to 6 mm, and by extrapolation a strength of 83.5 kv_{\max} per cm is obtained for 1-cm thickness and 133 kv_{\max} per in. for 1 in. thickness. There is no doubt that the strengths of samples 1 cm and 1 in. thick tested in air would very greatly exceed these values.

The impulse puncture strength under oil is much more nearly proportional to the thickness. The curve in Fig. 22 gives the relation:

$$V = (d/.0135)^{0.727}$$

where d is thickness in millimeters and V is puncture voltage in kilovolts. This gives a dielectric strength of approximately 150 kv per cm for 1-cm thickness and 300 kv per in. for 1-in. thickness.

There are very few published tests on thick sections with which to make comparisons. The authors of this book have many times obtained dielectric strengths exceeding 150 kv_{\max} per cm on samples of Pyrex electrical resistant glass insulators approximately 1 cm thick tested under dry oil with 60-cycle a-c voltage and values about 300 kv_{\max} per in. on 1-in. thicknesses. These higher strengths, which are about twice those of Inge and Walther, may be due to the different kind of glass used. Tests made in air on similar insulators having thicknesses of only 1 to 2 mm at the point tested gave puncture strengths 1000 to 1500 kv_{\max} per cm, which shows that the strength in air far exceeds the strength under oil. The voltages encountered in these tests were as high as 250 kv_{\max} , which was sufficient to cause considerable corona.

Warren²⁸ gave some data on "Pyrex Glass,"²⁹ "Lead Glass," "Lime Glass," and "Soda Glass." It is probable that the "lime glass" and the "soda glass" are of very similar compositions, if they were commercial glasses. His measurements were made in air on samples 50 mils thick (1.27 mm) most probably with 50-cycle alternating current with results expressed in effective volts. In order to have a comparison with the data previously cited his results have been changed to kilovolts (maximum) per centimeter and are given in Fig. 69.

The observations by Warren on "Pyrex glass" 1.27 mm thick, tested in air, showed a strength of 440 kv_{max} per cm or 1100 volts_{max} per mil on pieces 50 mils thick. This is not in agreement with the Corning result of 1000–1500 kv_{max} per cm on the same glass. In the Cor-

ning tests, the insulators were carried up to the flashover point at the rate of 80 kv_{max} per minute and held at the flashover voltage for 15 seconds unless puncture occurred in the meantime. The difference between these results and those of Warren must have been caused by the difference in corona action due to the different field distribution.

It is to be noted that the Warren data show a strength for "Pyrex glass"²⁹ at the "one-minute" mark of about 1.9 times that of the lime glass.

There seems to be no published information on the impulse strength of thick glass in air. Hence the authors of this paper are forced to resort to unpublished data furnished by the Corning Glass Works laboratory. This

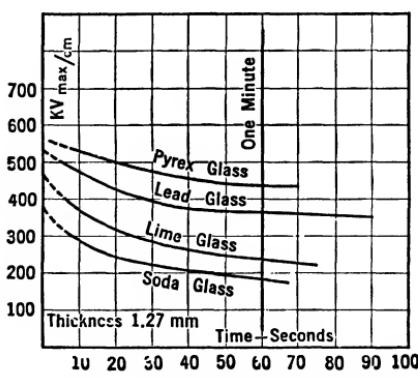


FIG. 69.—Dielectric Strength—Time.
After Warren.

²⁸ H. Warren, Electrician, 108, 286 (1932).

²⁹ This loose term probably means a Pyrex chemical resistance glass.

information is merely that Pyrex insulators approximately $\frac{1}{2}$ in. thick have withstood repeated discharges of a "lightning generator" at 1500 kv. The impulse time intervals and wave form are not stated. This gives a value in air of 1200 kv per cm without failure, as compared to the value, as cited above, of 150 kv per cm for another glass tested in oil. This difference is no doubt not due entirely to the difference between the two glasses, but also to the difference between the effect in oil and in air.

The lowering of strength previously cited as due to the heating effects of the conduction current and high frequencies were observed only on test samples having very large electrode areas compared to the thickness, a condition favorable to heating both by conduction and by dielectric loss. In practice, where insulators are used with high voltages, the condition is just the reverse. The frequencies are low in the case of power line insulators, and all insulators designed for high-frequency service are designed so as to have very low capacity and large thickness, so ordinarily there is no danger from either conduction currents or dielectric losses. High-capacity insulators for very high frequencies should be avoided or the material carefully selected and tested under conditions approximating service requirements, as the heating under such conditions might easily lead to failure.

In the case of special service such as is encountered in high-voltage cathode discharge tubes, the impact of discharge on the insulation should be avoided by proper design of the tube or by shielding, as this action may be destructive.

After consideration of the information discussed it appears that some glasses, so far as their dielectric properties are concerned, are well adapted to use in commercial insulators. There is no information on the effect of mechanical stress on dielectric strength, but it seems probable that the high dielectric strength of glass offers an ample factor of safety, provided the mechanical stresses do not approach the limit of resistance of the glass.

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